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PHASE TRANSFORMATIONS IN THE ACTINIDES[*]

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I. Introduction

The purpose of this review is to summarize and comment on the solid-state transformations that occur in metals that belong to the actinide series — in particular, plutonium and uranium, and to a lesser extent thorium, neptunium, and americium. Technologically, the two most important of these are, of course, plutonium and uranium, and much of what follows will be related to the information about these two metals. Both undergo a number of allotropic changes; plutonium is unique among metals in having six allotropic forms. The properties of metals whose crystal structure can be altered with relative ease under the influence of either temperature or pressure clearly depend on the detailed nature of the allotropic changes and their relation to the previous thermal and mechanical history.

It is known that some solid-state transformations are sluggish, some require large activation energies and thereby exhibit a strong temperature dependence, while still others may take place rapidly and at temperatures at which the availability or lack of long-range diffusion does not affect the reaction rate. Some transformations may require that a strict crystallographic orientation relationship exist between the new and the old phase, while others are not controlled by any such condition. Thermal activation, as a rule, introduces the time factor as an important parameter, but transformations that occur mainly by the displacement of lattice dislocations and without diffusion may, at least theoretically, occur at the speed of sound. Clearly, in all the stages of processing, using, and maintaining useful materials based on plutonium or uranium, a knowledge of many of the above features is very desirable.

In characterizing solid-state phase transformations in metals and alloys it is useful first to define several possible types of transformations. The terms commonly used to characterize structural changes lack universal acceptance. In part, this has arisen because of the different emphasis that may be placed on some specific features or parameters studied in a given transformation, such as diffusion, crystallography, morphology, kinetics, or thermodynamics. A martensitic transformation, for example, always involves a certain crystallographic relationship, but it is well known that in many non-martensitic transformations a crystallographic orientation relationship is equally important. Further confusion arises from the excessively used expression "nucleation and growth." It is not uncommon to find that this characteristic has been incorrectly interpreted as a criterion for the existence of a diffusional process and the absence of "shear"; but, fundamentally, all solid-state transformations must nucleate and grow, even though the particular details of the two processes may be quite different from one transformation to another.

Bearing in mind the above difficulties it will nevertheless be adequate for the purpose of the present article to define three general types of solid state transformations:

1) Diffusional nucleation and growth
2) Massive
3) Martensitic.

As a general rule, the first two can, if required, occur as isothermal transformations that proceed to completion at a constant temperature and depend to a varying degree upon thermal activation and diffusion. Martensitic transformations, on the other hand, usually occur only while the temperature is changing and as such depend only slightly, if at all, on thermal activation. They have been accordingly described as athermal transformations; but this particular classification becomes highly questionable, especially in the area of the actinide metals where some transformations, which possess general martensitic features, do occur isothermally, while others, which may involve considerable diffusion, reveal an athermal component. Furthermore, it is well known that it is possible for a polymorphic change to occur by a diffusional nucleation-and-growth (d-n-a-g) process under one set of conditions and by a martensitic process under a different set. The purity, the grain size, external stresses, and the rate of cooling or heating all play an important part.

Several types of low temperature transformations in plutonium, uranium, and their alloys can be usefully defined as martensitic even though they may occur isothermally. For this reason it will be helpful to amplify some of the features that will be emphasized in the subsequent discussion.

A martensitic transformation is one that occurs by a cooperative movement of many atoms. This means that the rearrangement of the atoms from the parent crystal structure to that of the product occurs by the passage of a mobile coherent or semicoherent growth interface and must therefore be assisted by the movement of specific dislocations and accompanied by transformation-induced lattice strains. It follows from the geometric features characteristic of a martensitic transformation that a specific orientation relationship between the product and parent crystal lattices must exist and a specific habit plane within the parent lattice is favored. Another feature is a shape change that must occur between the two lattices, with a specifically oriented shear component. While this is a consequence of all martensitic transformations, in many cases it does not follow that the necessary shape change should be easily detectable, nor that it can be expected as an easily identifiable disturbance of the free polished surface. On the contrary, when a large volume change occurs, the resulting surface disturbance may be completely unrelated to the shape change, a factor that may be of considerable importance with the large volume changes obtained with some of the phase changes in the actinides.

Diffusional-nucleation-and-growth transformations pertinent to this review may be considered to involve a thermally activated process related to the transfer of individual atoms across the transformation interface. Commonly, the transport of atoms occurs over many interatomic spacings and hence is related to the bulk diffusion. Such transformations should proceed isothermally unless a specific factor, such as a buildup of lattice strain, hinders them. There may or may not exist a specific orientation relationship depending on specific conditions, and the transformation interfaces may be incoherent, semicoherent, or fully coherent.

Transformations that are basically controlled only by the processes that occur at the transformation interfaces and therefore require only a very limited amount of diffusion are termed massive transformations.(1) In alloys, these types of transformations are also composition invariant, and in most cases the transformation interfaces appear to be incoherent. There is evidence that in massive transformations a crystallographic orientation interdependence between the two lattices is lacking. Massive transformations therefore nucleate with some difficulty but, once nucleated, may proceed with great rapidity, thereby inducing some possible plastic flow and acoustic effects. Massive transformations have been mentioned only briefly in the field of actinides, but it is clear that such transformations are quite likely to occur during allotropic changes that are, by definition, composition invariant. Recent studies of massive transformations have shown that because of their rapidity and lack of composition dependence, erroneous conclusions may be reached regarding their classification.

Despite the above enumerated difficulties, studies of many solid-state transformations have permitted each particular group of transformations to be associated with some features that are fairly characteristic of the group as a whole. This situation makes it desirable to be able in each new observed phase transition to decide what type of process is occurring. The identification of a transformation as a particular type should allow the general characterization of at least some of the parameters involved and hence allow greater control over some metallurgical features. Therefore, one of the main objectives of the present review will be an attempt to indicate the current status of the known transformations in the actinide series metals, using the three groups discussed above as a basis. It is well recognized that in addition to these three groups, a vast subdivision into various forms of transformations, known to exist in metals and alloys, is available in the literature. While the importance of these subdivisions increases as one moves from essentially allotropic changes to those occurring in various complex alloys, we do not propose to consider here any such additional subdivision. However, occasional reference will be made, where applicable, to particular cases such as bainitic transformations or those involving different degrees of order.

Given the numerous allotropic forms in the actinide metals, the total number of possible phase transitions, including some skip transformations, is quite large. A number of these are of particular technological or scientific importance, for example, the $\alpha \rightleftarrows \beta$ transformations in Pu or U; consequently, the literature on these transformations is quite extensive. Since this article is limited in scope we also do not claim that the quoted literature or the particular transformations that are discussed are in any way complete.

II. Some Specific Experimental Features

Studies of solid-state transformations in actinides constitute a special field because of the unusual experimental difficulties that are unavoidable when dealing with highly reactive metals, especially plutonium. Rapid surface oxidation, large volume changes during allotropic transitions, radioactivity, self heating, and high toxicity are but a few of the characteristic features that make many common metallurgical procedures difficult. For example, the helpful information that may be obtained from metallographic studies may be of little value because of the high degree of surface oxidation and surface rumpling. Likewise, the determination of crystallographic details, such as orientation relationships and habits, is made difficult not only because of the necessity of handling most samples under inert conditions, but also because the numerous allotropic transformations may preclude the possibility of preparing suitable single crystals.

Many important conclusions regarding the nature of each particular transformation, especially for Pu and Np have been drawn, therefore, from indirect studies such as transformation kinetics, differential thermal analysis (DTA), temperature of occurrence and thermal hysteresis, influence of stress and specimen size, thermal-athermal behavior, the temperature-time-transformation (TTT) behavior, presence or absence of surface shear, ultrasonic response or internal friction before and after transformation, and the like. We only refer below to a discussion on kinetics and to a few less conventional approaches.

A. Measurement of Kinetics

One of the objectives in the study of phase transformations is the ability to predict the overall reaction rates. However, our present knowledge concerning the phenomena of nucleation and growth is still too limited to allow the possibility of predicting the morphology, the rate of nucleation, and the rate of growth with the degree of certainty necessary for calculation of reaction rates from first principles. Therefore, as pointed out in a recent review,(2) the usual interest in understanding the general kinetics of a reaction stems instead from the possibility of extracting some valuable information concerning nucleation and growth from the measured overall reaction rates. This phenomenological approach to investigating the nucleation and growth involves two operations: (1) the experimental observation of the progress of a given reaction and

(2) the analysis of the kinetic data in terms of various nucleation and growth models. The measurements of the progress of a reaction are usually carried out by following the change of some macroscopic physical quantity — for example, length, electrical resistivity, internal energy, internal friction, volume, or sometimes density. It is then usually assumed that the observed property change is proportional to the volume transformed, which is of course an assumption that frequently requires specific justification. Even if the experimental data can be fitted into a homogeneous rate equation by properly choosing a certain set of constants, this practice merely facilitates the interpretation or extrapolation of the data, while the constants themselves may have doubtful physical significance. Apart from the mathematical difficulties, the real limitation of the indirect method for studying the details of a transformation through its kinetics is that the evaluated quantities are significant only if all the assumptions about the model are correct.

Isothermal kinetics data frequently have been analyzed using the Avrami equation:(3)

$$1 - x = \exp(-kt^n) \qquad (1)$$

or

$$dx/dt = nkt^{n-1}\,(1 - x), \qquad (2)$$

where x = fraction transformed, t = time, and k = temperature-dependent constant. Values for the exponent n, which may be claimed to give information about the type of nucleation-and-growth process, are obtained by plotting $\ln \ln \left(\frac{1}{1 - x}\right)$ vs ln t.

Special forms of the above equations, applicable to nucleation and growth processes under certain conditions, are due to Johnson and Mehl:(4)

$$1 - x = \exp[-(\pi/3)\dot{N}G^3t^4] \qquad (3)$$

or

$$dx/dt = (4/3)\pi\dot{N}G^3t^3(1 - x) = (4/3)\pi G^3t^3(dN/dt), \qquad (4)$$

where $\dot{N}$ is the rate of nucleation given by $(dN/dt)\,\frac{1}{1 - x}$, where N is the number of nuclei and G is the linear growth rate, dr/dt, assuming spherical particles of radius r. Equations (3) and (4) appear to be valid if the rates of nucleation and growth are constant and if the nucleation takes place at random in the form of spherical particles (of radius r) throughout the matrix. Thus, a value of 4 for the exponent n indicates that an isothermal transformation proceeding at constant rates of nucleation and growth is taking place, but of course the transformation could be diffusional or martensitic.

Avrami considered the decrease of the exponent n to be related to a morphological change from three-dimensional to one-dimensional particle growth. The nature of the nucleation rate was not considered in detail, but it seems that n can also be reduced under conditions where the initial nuclei are quickly exhausted and subsequent nucleation rate is negligible, as might be the case in a massive transformation. Under these conditions a value of n less than 4 may mean a different transformation mechanism rather than a different particle morphology. In the interpretation of n, the possible importance of nucleation behavior is frequently neglected.

B. Internal Friction and Relative Shear Modulus

The use of the internal friction measurements and the relative shear modulus as a method for distinguishing between martensitic and diffusional transformations has been proposed only recently$^{(5)}$ and is far from having been sufficiently tested. It appears that with certain transformations the internal friction above and below the transformation temperature changes very little and the shear modulus changes over a broad range, while with other transformations internal friction suffers a marked change and the relative shear modulus changes over a narrow range of temperature. The former are claimed to be the features characteristic of shear transformations and the latter of diffusional transformations. Apart from cobalt, the method has been tested only using transformations in Pu and U, whose nature is still open to question and, as discussed below, can often be variable, depending on conditions. For example, it was assumed for the purpose of calibration that the $\beta \rightarrow \alpha$ and $\delta \rightarrow \gamma$ transformations in Pu are martensitic, whereas the detailed discussion given below shows that the nature of these transformations, while being martensitic under certain conditions, clearly depends upon a large number of factors — for example, cooling rate, purity, thermal cycling, etc. In slowly cooled specimens (as done during internal friction studies) diffusional transformations would quite likely occur. Perhaps a more fundamental question regarding the use of internal friction measurements for distinguishing between transformation processes lies in the fact that there is no obvious reason why the behavior in the martensitic case should be more or less continuous (below and above each transformation temperature) and in the diffusional case discontinuous. Coherent or semicoherent matching across martensitic interfaces could perhaps produce a degree of coupling that might allow only a gradual change of internal friction, but since a change of structure is also involved during a martensitic change it is not at all obvious why internal friction should be almost independent of structure change. We feel that the method is as yet rather speculative but the observed behavior is certainly of interest. The use of internal friction in the case of Np$^{(6)}$ is discussed in the section dealing with this metal.

C. Acoustic Measurements

Measurement of acoustic emissions generated during phase transformations(7) provides another tool for testing the nature of transformations, because faint acoustic waves (of the order of 5 X 10^{-5} lb/in^2) can be detected that are likely to be associated with martensitic burst phenomena related to individual events. Such acoustic emissions have indeed been recorded during the $\alpha \rightleftarrows \beta$ transformation in Pu, possibly confirming the martensitic nature of the individual events, but it must be kept in mind that the method is sensitive enough to confuse "burst" phenomena with microcracking, grain boundary sliding, or discontinuous boundary motion such as may occur in some massive transformations. Nevertheless, the acoustic method, when well calibrated, seems to hold much promise for the future.

D. Isothermal vs Athermal Behavior

As mentioned in the Introduction, the terms isothermal and athermal are often used in the literature in connection with solid-state transformations. It may be worthwhile emphasizing that an isothermal transformation is one that can proceed at a constant temperature. In most d-n-a-g transformations, if a sufficient free energy difference exists to initiate a transformation, the process can proceed isothermally to completion. If the reaction becomes arrested it is because some opposing factor, such as lattice strain due to volume difference, reduces the driving force to zero. Under such conditions, further cooling may again restart the transformation, perhaps with an incubation period, because at the lower temperature the free energy difference is increased. Thus, a d-n-a-g transformation may become in a sense athermal, resembling the martensitic cases.

In the case of a martensitic reaction, the free energy difference is usually only sufficient to produce a very small amount of transformation at any given temperature and continuous cooling is required to bring the transformation nearer to completion under athermal conditions. It is clear that this need not always be the case, and if a martensitic transformation can occur under conditions when the lattice strain is continuously relieved, or is not substantial, there seems to be no reason why the process should not occur isothermally, assisted by thermal activation. Hence one can speak of shear transformations that possess isothermal features and of diffusional transformations that have at least partially athermal features. Under those conditions the terms isothermal and athermal lose their usual meaning and are of little help in distinguishing between different transformation processes.

It appears that some investigators may have excessively emphasized the athermal characteristics in the actinides with the implication that occurrence of an "athermal component" means martensitic behavior. On the contrary, most martensitic reactions in the actinides appear to be isothermal, with the uncommon (for martensite) features of incubation times, "C" curve characteristics, and related time components.

III. Transformations in Plutonium

In spite of the careful and time-consuming precautions that must be taken to avoid radioactive contamination when working with plutonium, significant strides have been made toward understanding the transformation characteristics observed in this metal and some of its alloys. The dimensional changes accompanying the various allotropic transitions and the approximate temperature ranges of stability for each of the six allotropes may be illustrated by the dilatometric heating and cooling curves shown in Fig. 1. The two curves were obtained with a vertical quartz-tube-and-push-rod dilatometer having a 5-g counterbalanced load. The Pu contained <200 ppm of impurities excluding Am, which was estimated not to exceed 190 ppm. Heating and cooling rates of 4.5°C/min were used. Although these rates are relatively slow, significant thermal hysteresis and differences in the general form of the curves may be noted for some of the transitions. The equilibrium transition temperatures are: 115 ($\alpha \rightleftarrows \beta$), 185 ($\beta \rightleftarrows \gamma$), 310 ($\gamma \rightleftarrows \delta$), 452 ($\delta \rightleftarrows \delta'$), and 480°C ($\delta' \rightleftarrows \epsilon$). Since in the pure metal a composition change is not involved during phase changes, it may be argued that any hysteresis effects may arise due to the particular type of transformation involved. For example, the majority of shear transformations generally require a large driving force, leading to a substantial temperature hysteresis.

Because of the large volume changes associated with many of the transitions (approximately 9, 3, 7, -0.4, and -2%, for the $\alpha \rightarrow \beta$, $\beta \rightarrow \gamma$, $\gamma \rightarrow \delta$, $\delta \rightarrow \delta'$, and $\delta' \rightarrow \epsilon$ transformations, respectively), large surface disturbances may be expected. Consequently, direct surface observation of some specific transformation features during or after each transformation becomes difficult. This is particularly true when several transitions have interceded between the preparation of a fresh surface and the examination of a given transformation. The crystal forms of the different allotropes are: monoclinic (α), bc monoclinic (β), fc orthorhombic (γ), fcc (δ), bc tetragonal (δ'), and bcc (ϵ).

There appears to be general agreement that the $\beta \rightarrow \alpha$ transition occurs by shear under a number of conditions; on the other hand, there is much controversy regarding the nature of the $\alpha \rightarrow \beta$ transition. Transformations at higher temperatures are mostly attributed to diffusion-controlled mechanisms, with the notable exception of the $\delta \rightarrow \gamma$ transition, which is believed to occur, at least in part, by a shear transformation. The "skip"* transformation $\delta \rightarrow \alpha$ is

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*In the accepted terminology a "skip" transformation is one during which the phase changes occur not in the proper sequence, but with one or two intermediate transitions being suppressed.

also generally believed to occur by shear. In what follows we consider each of the transitions in more detail.

A. The $\beta \rightarrow \alpha$ Transformation

By comparing the results obtained for Pu with certain features obtained for well-established martensitic transformations, a number of investigators have proposed that the $\beta \rightarrow \alpha$ transition occurs by a shear transformation. Many of the studies deal with the isothermal kinetics and cover a temperature range from about -95 to about 100°C.(8-18)

The data are usually presented in the form of isothermal transformation curves (% transformation vs ln time), TTT curves, or Avrami plots (ln ln $\left(\frac{1}{1-x}\right)$ vs ln time, where x is the fraction transformed). Examples for each of these plots are shown in Figs. 2, 3, and 4, respectively. The mechanisms proposed for the $\beta \rightarrow \alpha$ transformation in part resulted from interpretations of such plots.

One of the features of the $\beta \rightarrow \alpha$ transition that suggests a shear transformation (on cooling) is the presence of a significant temperature hysteresis.(9,11,14) The suggestion that an orientation relationship exists between α and β is made by Spriet(14) on the basis of some hot-stage metallographic observations of a specimen that was thermally cycled so as to cause only a partial $\alpha \rightarrow \beta$ transformation to occur on heating prior to the reversal of this transformation on cooling. Spriet refers to the similarities of the surface features before and after each cycle as evidence of a memory effect at the transformation interface.

1. TTT Studies. Even though the $\beta \rightarrow \alpha$ transformation may involve shear, it appears to be of the isothermal type, and numerous TTT studies have been reported. The minimum times (incubation times) prior to the start (or near start) of the $\beta \rightarrow \alpha$ transformation are temperature dependent and lead to a characteristic "C" curve. It may be noted that several of the studies indicate either two(9,17) or three(14,18) sets of the conventional "C" curves. Spriet(14) and Galerne and Spriet(18) conclude that the center region between about -80 and +50°C with a low activation energy of 2.6 kcal/mole must be associated with a shear transformation. The regions above and below the center region, which have an activation energy of some 11 kcal/mole, compared with an estimated value for self-diffusion in Pu of 16.5 kcal/mole, are attributed to diffusional mechanisms. This value, however, is obtained from the correlation proposed by Nachtrieb et al.,(19) in which the activation energy is related to the heat of fusion and the melting temperature. Such a value should then refer to ϵ-Pu and not necessarily to α- or β-Pu. The interpretation that these authors make on the basis of activation energies is therefore questionable. The characterization of the transformation according to the magnitude of the activation energy as either a diffusion or shear mechanism has been made by several

investigators and may have some general merit. Nelson and Shyne(20) point out, however, the difficulty of using activation energies derived from Arrhenius-type relationships by noting that these may be apparent rather than real. In general, the relationship between the derived values of the activation energy and the "C" curve behavior is not obvious because the activation energy, as derived from the time-temperature relationships, merely reflects the temperature dependence of a given process. The portion of the "C" curve above the knee describes a speedup of the process as the temperature is lowered and hence indicates a negative value of the activation energy — an untenable feature. Thus, the derived values may actually be related in some complex manner to the true activation energy as represented by a physical process that involves an activation energy barrier.

Rosen et al.,(9) using ultrasonic pulse techniques, obtained two distinct sets of "C" curves and argue that the two regions both involve displacive-type (martensitic) mechanisms. Their observations are interpreted according to the Knapp and Dehlinger model(21) for nucleation and growth of a martensitic product by the growth and expansion of dislocation loops. The region above about 35°C has a strong athermal component; the transformation does not go to completion. The lower temperature region exhibits isothermal behavior leading to completion. The athermal component is attributed to the development of high back stresses that build up during the progress of the transformation as a result of the volume change in the $\beta \rightarrow \alpha$ transition. At low temperatures the back stress is partly overcome by the increased driving force. The importance of the large free-energy difference necessary for overcoming the transformation stresses is also suggested by reheating experiments. A cessation of the transformation occurs on heating the specimens that were undergoing transformation from β to α at low temperatures. As the free energy difference diminishes nearer the equilibrium temperature, strains introduced by the prior transformation are then more effective in suppressing the continuation of the transformation. Spriet(22) suggests the presence of competitive diffusional and martensitic processes, which he discusses in relation to the schematic TTT curves reproduced in Fig. 5. Also included are the start curves for the $\alpha \rightarrow \beta$ transition, which is illustrated as being diffusional. Consistent with the overlapping of the lower curves, he concludes that the $\beta \rightarrow \alpha$ transformation occurs by diffusion at low cooling rates but is martensitic on quenching.

Davy and White,(17) by analogy with a double "C" curve obtained for steels,(23) which was interpreted in terms of massive and shear transformations for the upper and lower region, respectively, suggest corresponding processes for the double "C" curves obtained with Pu + 1.05 at.% Ti. The low activation energy of 2.4 kcal/mole at the lower temperatures suggests a diffusionless reaction.

Nelson's(12) work indicates that the discontinuities in the TTT diagrams, which imply the presence of "upper" and "lower" "C" curves, might be the result solely of the quenching technique. Several fluids with different quenching characteristics are usually used to reach the different isothermal temperatures. These fluids are also claimed to be unsatisfactory as quenching media. In some instances the discontinuities in the form of the TTT curve appear to occur at temperatures at which the quenching medium was changed. By contrast, using a single fluid (3M Company's FC-75, which has excellent quenching characteristics for the whole isothermal temperature range studied, -75 to +100°C) Nelson observed only continuous "C" curves for Pu with some 300 ppm impurities. Nevertheless, the discontinuities on individual isothermal curves obtained by Galerne and Spriet,(14,18) which are attributed to a change in the mechanism, cannot be discounted, at least on the basis of quenching media. Davy and White,(17) following experiments with Pu-Ti alloys, concluded that there was a progressive tendency for the single "C" curve to split into two "C" curves with increasing Ti content. This effect is illustrated in Fig. 6. It thus appears possible that the nature of the impurities present may account for the splitting of the single "C" curve.

2. Effect of Minor Impurities. A number of investigators(10-14,24,25) have concluded that an increase in impurity content results in an increase in the incubation period and a decrease in the transformation rate. Results obtained by Spriet(14) for 50% of the transformation of $\beta \rightarrow \alpha$, using Pu containing 200, 400, and 1000 ppm of impurities, are shown in Fig. 7. Explaining these results, he suggests(14,24) that since an increase in purity results in greater plasticity this should lead to a reduction in transformation stresses and also a related relaxation of these stresses with time and thereby facilitate the progress of the transformation. (It would be of value to be able to separate the effects of interstitials and metallic impurities. Unfortunately, only the total impurity contents are generally given.)

Davy et al. observed that Ti additions(8,17) retard, while those of Np(8) accelerate, the $\beta \rightarrow \alpha$ transformation relative to pure Pu. This difference was rationalized on the basis that Np is an α-stabiliser while Ti is not. Hafnium very substantially retards the $\beta \rightarrow \alpha$ transformation.(16) In general, it appears that alloying elements may have a pronounced retarding effect on the $\beta \rightarrow \alpha$ transformation; however, much additional work on controlled alloy additions must be done to clarify this question, especially the nature of the incubation period.

The "athermal feature" associated with the $\beta \rightarrow \alpha$ transformation (i.e., the lack of completeness) at temperatures generally above about 20°C has been noted by a number of investigators.(9-11,13,26) Nelson(13) observed quantitatively the extent to which the transformation remains incomplete in the athermal range by cooling specimens to -23°C that had apparently ceased to transform at higher temperatures. The results are reproduced in Fig. 8. The extent of incompleteness is given by the ratio $(W_q - W_f)/(W_q - W_i)$, where W_i and W_f refer to the sample weights in a fluid at the initial temperature prior to any transformation and at the apparent completion, and W_q represents weight following quenching to -23°C. For the particular Pu studied (500 ppm impurities) the highest temperature at which isothermal transition was still complete, without retained β, was about 25°C. Above approximately 25°C the amount of retained β increased progressively with increasing temperature. In a later report Nelson(25) observed that for a grade of Pu less impure than that used in the previous work the transformation was apparently completed in 10 days even at 75.5°C. On the other hand, for a poorer grade of Pu his results showed that about 40% of β phase was still retained after 125 days at 73.5°C and indicated that the transformation at this temperature would take years to complete. Thus, the apparent athermal behavior and, more to the point, the relaxation process permitting further transformation are strongly dependent on impurity content. Spriet,(24) in a similar vein, noted for Pu with 200 ppm impurities that the transformation goes to completion for temperatures up to 80°C; in contrast, for a metal of lower purity the upper temperature is reduced to 60°C. As noted earlier, he concludes that an increase in purity results in a reduction of transformation stresses and related relaxation of the stresses with time.

3. Transformation Stresses. The athermal component of the $\beta \rightarrow \alpha$ transformation is unquestionably associated with the stresses that develop as a result of the large volume contraction that accompanies this allotropic transition.(21,24,26-28) Spriet(26,29) discusses this question in some detail. First, he points out the necessity for distinguishing between mechanical stresses arising from the volume change accompanying the $\beta \rightarrow \alpha$ transition and the "crystallographic stresses" that cause strain hardening of the α phase. He suggests that the former are responsible for the temperature hysteresis and the athermal character of the kinetics; the latter affect the incubation period. He then proceeds to derive expressions for the magnitude of the stresses that develop, as a result of the volume change, for a spherical nucleus under both hydrostatic and nonhydrostatic conditions. In particular, he points out that the deformation and progressive strain hardening of the β matrix, involved in the $\beta \rightarrow \alpha$ volume change and in the introduction of the relatively hard α grains, cause the elastic limit of β to increase from 15 to about 60 kg/mm^2 during the transformation interval. Spriet suggests further that the transformation occurs simultaneously by diffusion and shear and that the shear component is induced by the stresses developed during the reaction. He concludes that this is consistent with the observation of Nelson *et al.*(30) that either externally applied uniaxial tension or compression raises the temperature for the martensitic $\beta \rightarrow \alpha$ transformation.

Liptai and Friddle(28) conjecture that, on the basis of the Clausius-Clapeyron equation, the transformation stresses, being tensile in nature, would lower the transformation temperature of the surrounding untransformed material and thereby inhibit further growth of the α phase. As transformation proceeds the stresses build up until plastic deformation of the remaining β phase occurs. We would expect that thereafter the rate of buildup of transformation stresses would be limited by the strain hardening of the β phase. Under conditions of hydrostatic compression the volume change due to the $\beta \rightarrow \alpha$ transition decreases from approximately 9% at atmospheric pressure to zero at about 54 kb.(28) Thus, an increase in external pressure (at least for hydrostatic compression) reduces the influence of the transformation stresses. As an example, this is reflected in the large decrease in the hysteresis temperature with an increase in pressure.(28,31)

The acceleration of the $\beta \rightarrow \alpha$ transformation, or the increase in the initial temperature at which it can occur following externally applied nonhydrostatic stresses, is well documented.(11,32-37) Such externally applied stresses also cause the formation of a highly textured structure(14,33,34,36-39) that can readily be observed metallographically. Under an applied uniaxial compressive stress the $\beta \rightarrow \alpha$ transformation proceeds by the formation of thin disk-shaped volumes consisting of many individual columnar grains of α in which the (010) planes are perpendicular to the direction of the applied stress.(34) The disks are perpendicular to the compressive stress, with the long axis of the grains perpendicular to the plane of each disk. Under a tensile load the disks form parallel to the direction of the applied stress. In the absence of an external stress the disks form randomly. The three possibilities are shown schematically in Fig. 9. A possible explanation for the formation of these disks is given by Ekbom and Bogegard(27) in terms of the stresses developed around an α grain due to the transformation volume change. The degree of texturing was found to be directly dependent on the applied pressure.(38)

4. <u>The n Coefficient in the Transformation Kinetics</u>. Nelson and Shyne(33) point out that martensitic transformations may display a variety of reaction kinetics and thus kinetic data alone are insufficient to establish whether or not the transformation is martensitic. For example, using Avrami-type plots Loasby and Lowe(11) obtained for the $\beta \rightarrow \alpha$ reaction values of $n = 2$ (60°C) and $n = 3$ (51 and 23°C), and hence interpreted the $\beta \rightarrow \alpha$ transformation as consisting of an initial formation of a fixed number of nuclei per unit volume followed by three-dimensional growth.

Judging by the fact that a massive transformation may be expected to involve an initial incoherent nucleation at suitable sites that are quickly exhausted, followed mainly by constant-rate growth, it is not unlikely that the transformation studied by Loasby and Lowe was, at least in part, massive. Values of the exponent n equal to 2 or less have been recently reported for some massive transformations.(40)

Nelson and Shyne(33) report a value of $n = 4$ for both the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transformations, which is consistent with a transformation proceeding with time-independent rates of nucleation and growth. This is to be expected for a transformation that requires thermally activated nucleation and growth but does not require alloy partitioning. This value of n is consistent with either a d-n-a-g transformation or isothermal martensite. But, as these authors point out,(20) kinetics alone are insufficient to describe the mechanisms involved, and hence there is an inherent weakness in the kinetic-measurements approach to transformation studies.

5. Effects of Applied Stress and Strain. Nelson and Shyne(33) probably present the strongest evidence, although still of an indirect nature, for concluding that the $\beta \rightarrow \alpha$ transition in Pu occurs by a shear transformation. They studied both the effect of prior deformation of the β phase and the effect of concurrent stressing during transformation on the kinetics of the transformation. Prior plastic deformation of the β phase, either by compression or tension, delayed the start of the $\beta \rightarrow \alpha$ transformation and decreased its transformation rate. This stabilization effect of the parent phase by plastic deformation is analogous to the so-called mechanical stabilization (delay in the martensitic transformation) that is readily effected in some Fe-Ni base alloys that have been deformed above M_d.* Figure 10 shows a comparison of the isothermal kinetics of the $\beta \rightarrow \alpha$ transformation for a deformed and undeformed specimen. If the reaction were diffusion controlled, the prior deformation should have accelerated the transformation.(41)

The results obtained on the effects of uniaxial stress on the start temperature of the $\beta \rightarrow \alpha$ transformation, for both compression and tension, are reproduced in Fig. 11. Nelson and Shyne suggest that, consistent with the interpretation given for steels,(42,43) the resolved applied shear stress aids the $\beta \rightarrow \alpha$ shear transformation to a greater extent than the normal tensile component, which is in opposition to the volume change, prevents it. With a compressive stress however, the normal component adds to the shear component. The two different effects are illustrated by the additional dashed lines we have included with the results of Nelson and Shyne in Fig. 11. Nelson and Shyne(33) also noted that highly anisotropic dimensional changes occurred on cycling a textured specimen without any applied stress. Assuming no temperature effects, the authors conclude that this anisotropic transformation strain can only be explained if the transformation occurs by shear and associated with it are crystallographic relationships.

6. Relationship Between Prior Thermal History and the $\beta \rightarrow \alpha$ Transformation. The starting β phase, prior to the $\beta \rightarrow \alpha$ transformation, may be obtained by either heating from the α region or

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*M_d refers to the maximum temperature at which martensite forms during plastic deformation of the parent phase.

cooling from the γ region; the β thus formed may be referred to as β_α and β_γ, respectively. The $\beta \rightarrow \alpha$ transformation from β_α is evidently considerably more sluggish than from β_γ.(12,34) For example, Nelson et al.(34) report incubation periods of 1000 and 5 min for β_α and β_γ, respectively, at 85°C; the corresponding maximum transformation rates observed at this temperature were 1.8×10^{-2}%/min and 1.5%/min, respectively.(34) These differences are attributed by the authors to the relative degree to which β_α and β_γ have been plastically deformed. In a transformation involving a volume change the weaker phase will deform to accommodate the harder phase. Since β is weaker than α but stronger than γ, the β_α will have undergone more plastic deformation than β_γ when it is initially produced. The results obtained are consistent with the observation that prior plastic deformation of β retards the $\beta \rightarrow \alpha$ transformation.(33) As the authors point out, this effect is characteristic of other isothermal martensite transformations.(43-45) Under external stress, either tensile or compressive, the transformation-start temperature is increased more for β_γ than it is for β_α. This may be expected because β_α should already be heavily deformed. An alternative explanation for the different behavior of β_α and β_γ can be related to grain size. The grain size of β_α is finer than that of β_γ.(46) For dilute alloys of uranium, in which martensite is also observed to form isothermally, it was shown(47) that a decrease in grain size of the parent phase retards the transformation. In addition, it is well known that, in general, martensite transformations are suppressed by a decrease in grain size. Thus, it may also be expected that the finer β_α grain size should yield a more sluggish transformation than that obtained with the coarser β_γ. An opposite behavior may be expected, however, on the basis of relative strengths. Since β_γ is stronger than β_α, the relief of transformation stresses should be more difficult in β_γ than in β_α and thereby oppose the grain size effect.

Several miscellaneous items may be mentioned with respect to the thermal history of the transformation. Lowering the transformation temperature results in a finer grain structure.(10,15) The final α grain size, however, appears to be independent of the way in which the prior β phase was obtained,(15) although the shape of the α grains apparently differ depending on whether formed from β_α or β_γ.(34) In contrast to the apparent lack of a β grain size effect on the α grain size, Liptai and Friddle(35) were able to obtain abnormally large α grains by transforming β to α under a hydrostatic pressure of 55 kb. At this pressure, the volume change between the β and α phases is near zero; the transformation takes place above 400°C, where grain growth may be quite rapid. It is quite possible, of course, that under those conditions the transformation is massive, which tends to generate large grains if incoherent nucleation is difficult.

Rosen et al.(9) noted, after cooling a Pu sample to room temperature following an isothermal hold at 88°C, that the structure consisted of a mixture of columnar grains with clusters of fine grains, the former forming at the hold temperature. They also noted that cycling through the $\alpha \rightleftarrows \beta$ transformation resulted in an extremely fine microstructure and a retardation of the transformation. Loasby and Lowe(11) also noted that cycling causes a retardation in the $\beta \rightarrow \alpha$ kinetics; the effect, however, does not appear to be much greater than that due to random variations between different runs. The fine microstructure was attributed to large plastic strains resulting from the repeated transformations. Spriet(29) concludes that the increased sluggishness of the transformation with thermal cycling results from strain hardening of the α phase. He states that the $\beta \rightarrow \alpha$ transformation temperature becomes lower with each cycle, tending towards a limit.(14) In contrast to these observations, Anderson et al.(32) observed that the transformation rate increased with thermal cycling. Considering that the transformation may occur either by a diffusive process or by shear, Spriet(14) concludes that the former process is operative on slow cooling, while the latter one is operative when the specimen is quenched.

It is evident from the above that much work remains to be done. In view of both the large volume change involved in the $\beta \rightarrow \alpha$ transformation and the pronounced influence of impurities, some of the common criteria applied as a test for distinguishing among different possible transformation processes are clearly inconclusive. The thermal vs athermal behavior is obviously inadequate, and so are probably activation energy values derived from Arrhenius-type relationships. Direct crystallographic data are meager, and metallographic features on polished surfaces are inadequate. The most convincing evidence for a cooperative shear process comes from the influence of externally applied stresses and plastic deformation. For reactions that involve substantial incubation periods the situation seems unclear. It is evident also that the mechanism of the transformation will depend on such additional parameters as sample size, rate of heating and cooling, and prior history.

B. The $\alpha \rightarrow \beta$ Transformation

Compared with that for the $\beta \rightarrow \alpha$ reaction, somewhat less definitive evidence exists that would permit the conclusive classification of the $\alpha \rightarrow \beta$ transformation. Largely on the basis of x-ray diffraction using fiber-textured α samples, Nelson and Bowman(48) proposed a correspondence relationship between the α and β lattices for the $\alpha \rightarrow \beta$ transition: $(010)_\alpha \parallel (\bar{1}11)_\beta$ and $[10\bar{2}]_\alpha \parallel [34\bar{1}]_\beta$, amounting to a combination of shear, rotational translations, and a shuffling of atoms. The relationship was in part substantiated by the observation that the 8.5% $\alpha \rightarrow \beta$ dilatometric expansion along the fiber axis for a textured α specimen was consistent with the 8.44% difference in the interplanar spacing expected between $(010)_\alpha$ and $(\bar{1}11)_\beta$ planes. Thus, according to the proposed model the (010) planes of α become members of the $\{\bar{1}11\}$ form of β. The fact that the $\alpha \rightarrow \beta$ transformation strains obtained on heating a highly textured α rod are greatly anisotropic,(33) also suggests the existence of some crystallographic correspondence between the two phases. In a remote way this favors the possibility that the $\alpha \rightarrow \beta$ transformation may be martensitic.

Selle and Focke,(49) by noticing that there was very little difference in internal friction just below and just above the transformation temperature for a number of shear transformations, concluded that both the $\alpha \rightarrow \beta$ and the $\beta \rightarrow \alpha$ transformations take place by shear. Spriet(14) notes that the transformation is dependent on prior thermal history; namely, the incubation period is significantly decreased if the α had been obtained by quenching instead of by a normal cooling from the β field. The subsequent time for completion of the reaction apparently is not affected. This might suggest the presence of some stress-induced nucleation caused by stresses resulting from the prior quench. Alternatively, if the presence of the additional quenching stress is not sufficiently important, then the difference in behavior might be related to the difference in the transformation mechanism corresponding to slow cooling or quenching. Furthermore, the opportunity to relieve any such stresses is greater under slow cooling conditions. Spriet(26) also makes reference to the presence of a surface memory effect obtained during a partial $\alpha \rightarrow \beta \rightarrow \alpha$ transformation; this would imply a reversible shear transformation. He also notes(14) that the growth of β is often blocked by α grain boundaries, which would suggest the existence of crystallographic correspondence in going from α to β as well as from β to α. In spite of these indications for the existence of a shear transformation, Spriet(14,26) concludes that the $\alpha \rightarrow \beta$ transformation occurs by diffusion particularly when it proceeds slowly — in times of the order of seconds. However, under very fast heating rates and only with the starting material being α of martensitic origin, the transformation itself may be martensitic.

1. Influence of Stress and Strain. Plastic deformation of the stable parent α phase by a 30 to 50% compression between 70 and 90°C, was observed to increase markedly the rate of the $\alpha \rightarrow \beta$ transformation.(33) This acceleration in the kinetics is consistent with the effect of deformation on diffusional transformations.(41) Even though small amounts of prior plastic deformation may favor a martensitic transformation,(45,50) large amounts of prior deformation are known to stabilize the parent phase in a martensitic process.(43-45) Thus, the effect of prior deformation observed(33) would suggest a transformation that does not involve shear. The application of stress while heating the sample during the $\alpha \rightarrow \beta$ transformation showed that tensile stresses lowered the transformation-start temperature to a much greater extent than the rise in temperature obtained from application of compressive stresses. This behavior is shown in Fig. 12. Since a transformation that involves a large volume increase is favored by application of a tensile stress, such results could be explained by considering that the transformation is of a shear type and that the shear stresses contribute to the progress of the transformation. In the $\alpha \rightarrow \beta$ case, however, the

contribution of the applied compressive stress opposes the transformation more by contribuiting to the volume strain effect than it apparently aids it by contributing to the transformation shears. Liptai and Friddle(28) state that, as β nuclei are formed on heating, compressive stresses are generated in the untransformed α, raising its transformation temperature. However, because of the relatively low strength of β, the temperature hystersis for the $\alpha \rightarrow \beta$ transition is much less than for the reverse action. The increase in the $\alpha \rightarrow \beta$ transition temperature by pressure has been observed during the rolling of β in the stable β range.

The apparent contradictory evidence given by the effect of prior deformation, namely that deformation promotes subsequent transformation, may be the consequence of a significant amount of recovery or recrystallization having taken place on heating α into the β region such that we are actually concerned with α being in a mild state of deformation. Nelson(37) observed that on annealing α specimens that had been compressed 40% in thickness, the material regained the transformation kinetics of the undeformed state by annealing for 2 weeks at 105°C. He therefore concluded that in deformed α only residual stresses remain, which then accelerate the $\alpha \rightarrow \beta$ transformation.

Bodine <u>et al</u>.,(51) although only in a single test, showed that an applied tensile stress of 11,900 psi at 123.5°C did not affect the start of the $\alpha \rightarrow \beta$ transformation. This is surprising in view of the results reported by Nelson and Shyne,(33) who showed that the tensile stresses applied while heating a sample at a rate of 2°C/hr lowered the transformation-start temperature 0.6°C per 1000 psi. For a stress of 11,900 psi this corresponds to about 7°C. Such a large effect should be reflected in an increase in isothermal transformation rate. The authors also conclude from analysis of their tensile data obtained by testing α in the β region (118 to 124°C) that there was no evidence for strain-induced transformation of α to β. The results of Bodine <u>et al</u>. do not necessarily support or deny any specific mechanism, but they are clearly in contradiction to the strong effects of stress and strain reported by others.

2. <u>Studies of Kinetics</u>. In agreement with Nelson and Shyne,(20) Spriet(14) considers the $\alpha \rightarrow \beta$ kinetics to be typical of a d-n-a-g transformation. In the vicinity of the equilibrium temperature the transformation exhibits an athermal behavior,(14,22) which, as for the case of the $\beta \rightarrow \alpha$ transformation, arises from the transformation stresses. The influence of internal stresses on the $\alpha \rightarrow \beta$ transformation has been considered in some detail.(26) The approach used is similar to that briefly described earlier for the reverse transformation. Spriet(14) considers that the increase in the transition temperature, i.e., the departure from equilibrium, is determined by the hydrostatic pressure created by the formation of the nucleus. Thus, since an increase in purity allows for greater plasticity of the α and therefore a relief of this pressure, a

considerable decrease in the incubation time and a lowering of the transition temperature are obtained. In addition, the activation energies decrease; they are 33, 28, and 21 kcal/mole for 1000, 400, and 200 ppm of impurities, respectively.(14) These high values do suggest a diffusion-controlled mechanism and in the purer material are not unlike the values for a massive transformation. The large change in activation energy with impurity content does imply that the relative solubilities of the impurities in the two phases may be important in affecting the kinetics. However, as was pointed out earlier for the $\beta \rightarrow \alpha$ transformation, Nelson and Shyne(20) question the use of activation energy values for the $\beta \rightleftarrows \alpha$ transitions as possible indicators of the mechanisms involved in these transitions.

Faiers et al.(52) studied the kinetics of the $\alpha \rightarrow \beta$ transformation by resistance heating of wire specimens — noting the start and finish times during the continuous heating — covering heating rates between about 1°C/min and 7×10^3°C/sec. They obtained non-isothermal transformation curves in the 120-230°C temperature range. They point out that their data are in disagreement with those generally reported by others. For example, at 140°C their results and those of Spriet(14) for both the start and finish times differ by a factor of nearly 10^6; however, the comparison is made between non-isothermal and isothermal measurements, respectively. One would expect that the former would yield somewhat shorter times, but not to such an extent. Faiers et al.(52) attribute the differences observed to the large decalescence effect. The heat of transformation for the reaction is approximately 900 cal/mole.(53) The heat transfer in an oil medium, which is usually employed, would be too slow to maintain the proper specimen temperature, especially for short times; and, since the reaction is strongly temperature dependent, a drop in temperature would yield apparently long times. With resistance heating this problem would most likely be absent. These authors do not speculate on the transformation mechanisms. Loasby(54) also notes considerable decalescence in studying the $\alpha \rightarrow \beta$ transformation of foils. The temperature at the end of the transformation is 10°C below that at the start, and he proposes that in going from slow to fast heating rates (the use of oil baths to resistance heating) the transformation mode changes. He suggests that with resistance heating localized hot spots are formed from which shear-type growth is initiated.

Nelson, in some early studies(15) reported on the isothermal behavior obtained at several temperatures between 123 and 150°C and noted that the isothermal curves for the $\alpha \rightarrow \beta$ reaction were similar to those obtained for the $\beta \rightarrow \alpha$ transformation. Hill,(55) in determining the equilibrium $\alpha \rightleftarrows \beta$ and $\beta \rightleftarrows \gamma$ transition temperatures, noted that for both transitions the formation of β takes place more readily than do either of the reverse transformations. The implication here is that $\alpha \rightarrow \beta$ and $\gamma \rightarrow \beta$ are more temperature sensitive than are the $\beta \rightarrow \alpha$ and $\beta \rightarrow \gamma$ transitions.

The effect of alloying on the $\alpha \rightarrow \beta$ transformation has been examined(8) for a Pu-0.90 at.% Ti alloy and a Pu-1.3 at.% Np alloy. Ti accelerated while Np retarded the reaction relative to that for the unalloyed Pu. Exceptionally high activation energies were reported: 182.4, 226.0, and 166.8 kcal/mole for the unalloyed, Np-alloyed, and Ti-alloyed materials, respectively. The authors do not suggest any mechanism or offer any reason for the large discrepancy between their values for the activation energy and those reported by Spriet.(14)

In attempting to interpret the kinetics in terms of the Avrami equation, Spriet(22) observed for the $\alpha \rightarrow \beta$ transformation a value for n = 1.7; and, since a mechanism could not be related to such a value, he concluded that the Avrami equation had to be modified to take into account the transformation stresses. He adopted the calculation used by Burgers and Groen(56) for the transformation in tin, which, with the assumption that the rate of nucleation is a linear function of x, is of the form

$$\frac{1}{1 - x} \frac{dx}{dt} = nk\,(1 + px)\,t^{n-1}, \tag{5}$$

where k (1 + px) has replaced the k in Eq. (1). The parameter p is assumed to be a temperature-dependent constant that represents the effect of internal stresses on the rate of nucleation.(24) The results obtained with this approach suggested that the stresses accelerate the kinetics as the temperature increases. This argument is difficult to follow, for one may expect instead that the increase in temperature would result in the stress factor being less important, since with an increase in temperature recovery can occur more readily and the free energy driving force becomes greater. Nelson and Shyne,(20) by monitoring the changes of specific volume in 0.4-mm thin wafers of Pu and using the Avrami equation, obtained a value of n = 4 for the $\alpha \rightarrow \beta$ transformation, in contrast to the 1.7 obtained by Spriet. They point out that erroneous values for n can readily be obtained when the transformation stresses are treated by means of an additional parameter p, since p is an adjustable parameter that depends on the choice on n. Spriet,(24) in a later paper, concludes that his earlier work does not contradict the results of Nelson and Shyne because he was also able to obtain a value of n = 4 for high purity Pu (200 ppm), for which the kinetics are practically independent of stresses. However, for a metal of intermediate purity (400 ppm), n was found to change from 1.7 at 125°C to 4 at 160°C. In the latter work, however, Spriet did not involve the parameter p in his plots.

For the $\beta \rightarrow \alpha$ transformation Spriet's analysis(22) yields negative values of p, which vary from -1 at 19°C to -1.7 at 73.5°C. This implies that the transformation is always hindered by internal stresses and that this factor becomes more important as the temperature increases. Such behavior is to be expected, for the free-energy driving force decreases on approaching thermodynamic equilibrium, and then the contribution of stress can become more significant.

3. The DTA Anomaly Preceding the $\alpha \rightarrow \beta$ Transformation. A curious anomaly that may appear during the heating of α, which has not as yet been satisfactorily explained, has been noted by several investigators.(29,57-61) Depending primarily on the prior thermal history of the test sample, a small heat effect may be detected prior to the large heat absorption obtained for the normal $\alpha \rightarrow \beta$ transition. The phenomenon has been called a "pre $\alpha \rightarrow \beta$ transformation"; but this terminology assumes that a phase change does indeed take place here, a fact not yet conclusively established. Both the interpretation of the experimental DTA data and the explanations given for the observed behaviors are controversial. A typical DTA anomaly is shown in Fig. 13 for a high purity Pu sample.(61)

The DTA curves obtained by Pascard,(62) Spriet,(29) Ludemann,(61) and especially that by Selle and Etter(58) (see Fig. 14), show the anomaly as a heat absorption. In contrast, the data of Harbur et al.,(60) instead of indicating a heat absorption, clearly reveal that a heat evolution occurs below the normal $\alpha \rightarrow \beta$ transition temperature; on the basis of DTA, resistivity, and density measurements they ascribed the anomalous behaviors observed to the transformation of retained γ. They propose that the transformation stresses, introduced on cooling from the γ field, prevent the completion of the decomposition of γ. On reheating, these stresses are relieved and thereby permit further transformation of γ to occur, first to α and then to β, with each reaction accompanied by a heat evolution below the normal $\alpha \rightarrow \beta$ transition temperature. The authors(60) noted that on the initial heating of an α-stabilized specimen such heat affects were not detected. After the specimen is cycled into the β field, these effects were still absent. However, if the specimen were cycled into the γ field, then the heat effects were obtained on reheating. The authors finally conclude that the apparent exothermic behaviors observed by others are in reality the cessation of the $\gamma \rightarrow \beta$ exothermic reaction.

Although the results obtained by Harbur et al.(60) are self-consistent and indeed convincingly support their conclusions, their interpretations are inconsistent with some of the observations made by others. Selle and Etter(58) reported that they could eliminate the phenomenon by the use of two different prior thermal treatments, one involving an anneal and the other a quench; neither one of these should (necessarily) lead to the formation of an all-α specimen. On reheating such a specimen, following the reverse $\beta \rightarrow \alpha$ transition the pre $\alpha \rightarrow \beta$ effect reappeared; furthermore, additional cycling (between α and β) did not eliminate it. It is difficult to conceive how the $\gamma \rightarrow \alpha$ or $\gamma \rightarrow \beta$ transformations could be present here. In contrast to the results of Selle and Etter, Spriet(29) shows that the effect is eliminated after cycling. One may suppose that γ was originally present in the specimens on first heating; and, in fact, the pre-endothermic-like step shown by Spriet, Ludemann, and Pascard could possibly be interpreted as proposed by Harbur <u>et al</u>. However, it is difficult to ascribe the shape of the endothermic-like peak obtained by Selle and Etter to a cessation of a prior exothermic reaction, especially the appearance of a definite sharp minimum between the anomalous and expected heat effects, as shown in the trace in Fig. 14.

Interestingly enough, proponents of both the exothermic and endothermic interpretations attempt to ascribe the origin of the anomalous behaviors observed, at least in some measure, to a stress effect. The retention of the γ phase has been noted in the above. Spriet(29,57) and Liptai(59) attribute the anomaly to a stress-induced $\alpha \rightarrow \beta$ transformation, whereby the transition temperature is altered in accordance with the Clausius-Clapeyron equation. On first forming the less-dense β, the transformation tensile stresses from the prior cooling transformation are sufficiently stress relieved and new compressive stresses develop so as to bring about a cessation of the transformation until a higher temperature is reached. This is consistent with the known effects of hydrostatic pressure of phase transitions in Pu.(28) One may also suggest that the anomaly (if exothermic) could also be attributed to the transformation of retained β to α. Selle and Etter(58) argue against a stress-related transformation on the basis of prior annealing treatments not affecting the temperature of the pre-effect. On examining several alternative possibilities, they conclude that the anomaly is mainly due to the relief of stresses caused by the formation of microcracks. It is difficult to see why these cracks should form at the elevated temperatures (in preference to some low temperature). Furthermore, the energies involved would be difficult to detect relative to that for the normal $\alpha \rightarrow \beta$ transition and, in any event, would be exothermic for a stress relief.

It has been noted(57) that increased purity lowers the pre $\alpha \rightarrow \beta$ transformation temperature region. If this behavior is indeed related to residual γ, an increase in purity should also exhibit a parallel trend for the effect attributed to the γ phase. It is also interesting to note(58) that additions of only 0.1 at.% of either Al, Si, or Ga (elements that exhibit solid solubility in the high temperature phases) eliminated the above-mentioned anomalous behaviors. Other elements (Fe, Ni, Co, Mg, Cu) apparently did not have any effect. Again it would be of interest to see whether a parallel behavior is to be obtained for experiments involving retained γ. For example, do small Al, Si, and Ga additions disfavor the retention of the γ phase? It appears to us that this rather controversial curiosity is far from being unequivocally explained, as is implied by Harbur et al.(60) The use of concurrent x-ray diffraction may provide an explanation.

C. The $\delta \rightarrow \gamma$ Transformations

The $\delta \rightarrow \gamma$ transformation behavior has been studied extensively by dilatometry; a typical behavior is shown in Fig. 15. On continuous cooling, two distinct regions are observed on a dilatometer trace.(14,63-68) The detectable start of the $\delta \rightarrow \gamma$ transition is indicated by a sharp discontinuity (at point B), whereby the expansion due to the cooling of δ suddenly changes to a contraction; over a further temperature drop of some 50°C the contraction continues wihtout any discontinuities (between B and C). The next region (at still lower temperatures) is characterized by a series of successive steps, i.e., abrupt discontinuous contractions (between C and D). This burst-like behavior, which is also indicated by the presence of a corresponding sequence of sharp peaks in DTA curves,(14,62,63) has led to the general belief that the $\delta \rightarrow \gamma$ transition, at least in this region, occurs by a shear transformation. The hysteresis temperature range — between the equilibrium transition temperature and the first discontinuity — is considered by Pascard(63) as an additional transformation region, which he refers to as an "inactive region" between A and B. This term is inappropriate, since extensive transformation can occur in this region either under isothermal conditions or at very slow cooling rates. Pascard refers to the three temperature ranges as regions I, II, and III, corresponding to successively lower temperatures, respectively (see Fig. 15). This system has been generally adopted.

The presence or absence of any of the above described regions and the temperatures ranges over which they appear are sensitive to both prior thermal history and cooling rate.(65,67-69) Although Pascard(63) suggested that the start of region II (286°C) was insensitive to cooling rate, Taylor(65) on the basis of his results suggests that at sufficiently slow rates the start of region II would occur some 25°C above this temperature. The transformation has been observed to go to completion at temperatures within about 35°C of the equilibrium temperature 310°C, i.e., in Pascard's region I, without any indication of martensitic bursts, although in this range it may require of the order of 200 to 300 hr for completion. Hocheid et al.,(67) on comparing results obtained with two cooling rates, 6 and 80°C/sec, concluded that a decrease in cooling rate results in a widening of the temperature range and an increase in the amount of transformation in this region. The finish temperature of region III (i.e., point D) apparently is not affected by the rate of cooling. Taylor(65) notes that the start of the $\delta \rightarrow \gamma$ transformation could be suppressed to 250°C for a maximum cooling rate of 53°C/min. Using much faster cooling rates, ranging from 20 to 5000°C/sec, Faiers and White(71) noted a continuous decrease in the transformation temperature from 225 to 150°C. These studies were made by quenching wire specimens with helium gas and noting the arrests on thermal cooling curves. Only single arrests were observed.

Hocheid et al.(67) noted that, if a sample had previously partially transformed in region II and was then reheated into the δ range, on subsequent cooling it would exhibit a considerably larger amount of transformation in region II than in a specimen that had previously been continuously cooled so that it had transformed in both regions II and III. Continued cycling at a rate of 140°C/hr through the $\gamma \rightarrow \delta$ transition did not effect any changes from one cycle to another. Hill(69,70) observed that if a sample was thoroughly annealed in the δ range (9 hr at 380°C or 2½ hr at 420°C) the onset of region II could not be defined. He suggested that embryos required for the abrupt initiation of this region were eliminated, although martensitic jumps still appeared. In view of these observations(67-70) it would seem that a memory effect — a remnant of the structure of the γ phase and in particular how it was formed — is carried into the δ region, which, if not eliminated, influences the reverse $\delta \rightarrow \gamma$ transition. However, the characteristics of the $\gamma \rightarrow \delta$ transformation obtained on heating, which has received very little attention and was considered to be diffusional,(49) are apparently not affected by the prior history.(67,68)

Hocheid et al.(67,68) suggest that an explanation for the effect of thermal history lies in the distribution of the impurities. During the isothermal transformation in region II, partitioning of the impurity elements takes place. Except for long times or high-temperature anneals, this partitioning is not completely eliminated on heating into the δ range. Thus, on subsequent cooling, the diffusion-controlled component of region II can more readily take place prior to the start of region III. The latter largely involves a martensitic reaction not concerned with any solute partitioning. This argument is consistent with the observation reported by Spriet(14) that on repeated cycling using slow rates the transformation proceeded more and more in region II, whereas with fast rates the extent of the transformation regions was unaffected by cycling. He observed precipitates in δ as a result of cycling and suggested that the slow cycling caused repeated purification of the solid solution — i.e., by solute rejection. This implies that the purer the metal the more likely will the transition take place by isothermal mechanisms rather than by athermal (martensitic) ones — on continuous (moderately slow) cooling. Pascard(63) also claims that the amount of γ formed in region II is affected by impurity content. His conclusion, however, is based on only a few tests, about which little information is presented.

The characteristics and magnitude of the isothermal kinetics reported by Pascard(63) differ significantly from those obtained by Taylor.(65) For example, interpolation of the curves given by both investigators shows that, on holding for 24 hr at a constant temperature of about 240°C, Pascard and Taylor obtained approximately 7 and 80% transformation to γ, respectively. Whereas the curves given by Pascard show a constant rate of transformation following a rapid initial decrease, a nearly linear behavior is obtained by Taylor with a semilog plot. If Pascard's data are plotted on a semilog basis, the initial portion of a sigmoidal curve is obtained, typical of a three-dimensional nucleation and growth mechanism. In contrast, the three relatively flat semilog curves obtained by Taylor are more typical of either a one- or two-dimensional type of growth, indicative of an acicular formation(3) such as may be obtained for a martensitic transformation.

An examination of the steps in region III reveals that the behavior along the "arrest" portions shows a contraction that is greater than that accounted for by the presence of a fixed amount of δ and γ phases.(64) Thus, transformation must be taking place between the bursts as well as during the burst, indicating that even during continuous cooling through region III two mechanisms (both perhaps martensitic) may be operative.

Spriet(14) observed the surface of a sample of Pu as it cooled from the liquid state. The δ → γ transition was characterized first by surface undulations, then by surface striations (shear markings), and finally by abrupt spurts. On the basis of these observations he concludes that both diffusion and shear mechanisms are operative. Using dilatometry with cooling rates between 5 and 2500°C/hr, he constructs an anisothermal TTT that suggests under what cooling conditions one or both of the two mechanisms would be operative. With very rapid cooling rates (>2500°C/hr) a completely martensitic (shear) transformation is indicated.

The results of Faiers and White,(71) referred to earlier, are in agreement with this conclusion in that they observed only single arrests; the slowest cooling rate they used was 20°C/sec (72,000°C/hr). However, whereas Spriet's(14) TTT diagram indicates athermal behavior for the shear transformation, Faiers and White show in contrast a strong temperature dependence on cooling rate. Whether this should be regarded as d-n-a-g, isothermal martensite, or massive is, of course, open to question. Spriet(14) also shows, on repeating his work with a high purity metal, that an increase in purity results in shifting the transformation lines in the "diffusion-controlled" range to shorter times and shifting the M_s to a higher temperature. Although the former shift is consistent with the arguments presented that increased purity facilitates the diffusion-controlled transformation of region II, the upward shift of the M_s is contrary to what has been described in the above if the M_s is taken as the start of region III (point C). As a point of interest, it may be noted that the skip transformation δ → β is shown as interrupting the end of the martensitic δ → γ reaction for intermediate cooling rates.(14)

Thus, although there appears to be reasonable evidence that the δ → γ transition can occur by either a shear or a diffusional mechanism, Pascard,(63) in the early investigations, and Selle and Focke,(49) more recently, consider that the transition is entirely martensitic. Selle and Focke base their conclusion on internal friction and modulus changes observed across the transition temperature, but we feel that these particular criteria have not yet been sufficiently tested. Pascard's conclusion was based at least in part on the fact that the temperature ranges of the different transformation regions were apparently insensitive to the cooling rates they employed (although the rates used varied only by a factor of 4) and that during isothermal transformation, after an initial rapid decrease, the subsequent transformation rate was constant. He therefore suggested that the transformation occurs by the formation of martensitic platelets of γ accompanied by the buildup of constraints, leading to a retardation of the martensitic process. Subsequent transformation then depends upon (thermally activated) stress relaxation, which becomes the rate controlling factor. He attributes the different regions (I, II, and III) to the relative sizes of these platelets -- the increased supercooling providing a larger driving force and thereby leading to increasingly larger size platelets. Thus, he considers the steps in region III to be due to the crossing of grain boundaries of platelets as a series of avalanches resulting in "macroscopic jumps."

Considering the transformation as a martensitic one, Pascard(63) proposes a possible lattice correspondence between the two phases, namely, $(111)_\delta \parallel (100)_\gamma$ and $[110]_\delta \parallel [100]_\gamma$. He concludes that although the δ → γ transformations are martensitic at all temperatures they do differ in some aspects. In sharp contrast to this, Hill(70) concludes that the transformation has a martensitic character below 200°C, a non-martensitic character above 285°C, and an overlapping property between these two temperatures. The observations reported here would appear to be more in agreement with the conclusions of Hill than with those of Pascard, although the temperature ranges proposed must depend on cooling rates and purity.

D. The δ → α Transformation

As is well known, the δ phase of Pu can be stabilized to room temperature by the addition of several atomic percent of one of a number of alloying elements, for example, Al, Am, Ce, In, or Ga. Nevertheless, depending on the extent of alloying, the transformation of δ to α can be made to occur on cooling to subzero (°C) temperatures,(14,52,54,72) or by subjecting a sample to plastic deformation(14,52,73) or hydrostatic compression.(74) It is generally proposed that the δ → α transition in these alloys occurs by a shear process,(14,52,72,75) but there is also evidence that a massive transformation is possible.(52,54)

A correspondence matrix between the two crystal lattices, α and δ, has been suggested by Lomer(75) for a Pu-5% Ce alloy. Lomer's description permits the construction of a unit cell of the α structure, containing 16 atoms per cell, from 4 unit cells of the δ structure, each having 4 atoms per cell. The suggested strain matrix achieves this structural change with only very small additional atomic displacements. Following Lomer's work, Spriet(14) has described a homogeneous shear in the δ structure that, with limited atomic readjustments, would achieve the α structure.

Spriet(14) reports the appearance of a "feathery" structure, characteristic of martensite, on deforming a δ-phase Pu-2 at.% Al alloy. When another specimen was cooled in liquid nitrogen, the formation of platelets of α could be seen, again suggesting a martensitic transformation.

Elliott et al.,(72) in studying the resistivity of a series of δ-stabilized alloys at subzero temperatures, noted the identical temperature dependence of resistivity for both δ and α. This suggested to the authors that in some way the two phases are quite similar to each other, including perhaps their electronic structures. For compositions of intermediate stability the transitions at subzero temperatures were found to be reversible with a hysteresis of about 100°C. Elliott et al. feel that, in spite of the different crystal structures, from the point of view of symmetry there may exist a simple transformation mechanism, possibly by shear, to account for such reversibility.

1. Strain-Induced Transformations. Elliott and Gschneidner(74) studied the progress of the decomposition of δ as a function of hydrostatic compression. For the Pu series alloyed with Al, Zn, or In, compression-induced transformation occurred only at low alloy contents when the δ fcc structure transformed (irreversibly) to α or to a mixture of $\alpha + \beta$. Maximum pressures close to 10,000 atm were used. For the Pu series alloyed with Ce a double transformation was obtained, which for low Ce contents was irreversible; the δ phase transforms first to β (+ some γ) at the lower pressures, while at higher pressures the β (+ some γ) in turn transforms to α. For Ce contents in excess of 7.1 at.% the $\delta \rightarrow \beta$ transition occurred and was found to be reversible; for Ce contents in excess of 16.3 at.% both transitions were believed to be reversible. In general, the extent of reversibility increases with increasing Ce content. The authors noted that for a 4-at.%-Ce alloy the β-phase microstructure resembled a martensitic product.

Hambling et al.(73) studied the influence of uniaxial compressive deformation on strain-induced decomposition of δ at a series of temperatures between 23 and 180°C. The extent of transformation was determined by room-temperature density measurements; the authors claimed that the effect of cycling from the test temperature to the measurement temperature was minor. The compositions chosen (0.85 at.% Al, 0.85 at.% Ga and 2.2 at.% Ce) were such that δ could only be retained down to room temperature by a rapid quench. In contrast to the results cited above by Elliott and Gschneidner (for Ce and Al additions), these authors observed that the transformation of δ to α generally proceeded through the formation of γ. They suggest that the difference in the transformation sequences is due to the presence of shear stresses under their test conditions, which are absent during hydrostatic compression, thereby implying that the $\delta \rightarrow \gamma \rightarrow \alpha$ sequence occurs by shear and $\delta \rightarrow \beta \rightarrow \alpha$ perhaps does not. On the basis of density and x-ray measurements, Hambling et al.(73) propose that in the Pu-Al alloy concurrent transformations of $\delta \rightarrow \gamma \rightarrow \alpha$ occur, while in the Pu-Ce alloy these transformations occur consecutively: $\delta \rightarrow \gamma$ and $\gamma \rightarrow \alpha$. The curves showing the change of density as a function of deformation exhibit different characteristics for the three alloys; and, furthermore, for any given alloy distinct regions can be seen. As an example, the results for the Pu-Ce alloy are shown in Fig. 16. It would appear that new insight might be gained by devising experiments that would explain the observed differences. The authors point out that the x-ray results were representative only of the surface, which, they suggest, may be quite different from the interior. In addition, although some β was indicated in two of the Pu-Ga specimens, they discount its presence and conclude that for this system the transformation proceeds directly from δ to α.

Faiers et al.(52) showed the presence of strain-induced transformation of δ to α on cold rolling a Pu-1.5 at.% Ga alloy; the amount of transformation increased successively on going from 0 to 50 to 75% reduction. Deformation also caused increased amounts of transformation (from δ to α) to occur during thermal cycling between subzero and elevated temperatures.

2. Transformation Kinetics. The athermal and isothermal characteristics of the $\delta \rightarrow \alpha$ transition, as determined by density measurements, are seen in the results reported by Faiers et al.(52) For a Pu-0.85 at.% Ga alloy the transformation curves are sigmoidal between -60 and 0°C. Both the rate of transformation and the extent of transformation (leveling off) increases markedly with the lowering of the isothermal temperature. The resulting TTT-"C" curves obtained are shown in Fig. 17. On cooling to -80°C (quenched into a silicon fluid bath cooled by solid CO_2) the transformation began before reaching the bath temperature and quickly reached a value of about 50% transformation; thereafter it proceeded slowly to a maximum value of about 55%. However, still larger amounts of α could be induced by cycling between -80 and 25 or 100°C. The amount formed increased with each cycle, larger amounts being formed with the higher maximum-temperature cycle. The results are shown in Fig. 18. The data for curve C shows that the amount of transformation obtained by cycling between 25 and 100°C is negligible. In addition, no evidence of a time dependence at the higher temperature was found. Similar results were reported for higher Ga contents (up to 2.3 at.%) except that the transformation kinetics were markedly retarded with increasing Ga contents. The authors admit that their studies do not permit the mechanism involved to be clearly defined; but, they suggest that because of the low temperatures the transition would be expected to occur by either a shear or a massive transformation. They propose that the isothermal behavior is associated with a thermally activated nucleation and/or discontinuous growth and that the arrest of the

transformation is due to the buildup of accommodation stresses at the interphase boundaries. On thermal cycling the stresses are relaxed during the high temperature leg, allowing further transformation to take place at the lower temperature.

3. Evidence for a Massive Transformation. An interpretation suggesting a possible massive transformation stems from the work of Ward.(76) For a 1.5 at.% Ga alloy examined at -75°C, he noted the formation of nodular areas of irregular-shaped boundaries growing continuously and across the δ boundaries. He also noted a second interface moving across a region already transformed, suggesting a possible two-stage process. Faiers et al.,(52) describing what they call "preliminary metallographic evidence" on examining a transformation for a 1.5 at.% Ga alloy over a $2\frac{1}{2}$-hr period at -70°C, noted the formation of large nodular regions with irregular boundaries that underwent very slow time-dependent growth. On this basis they proposed a massive transformation but did not exclude the presence of a martensitic mechanism at other temperatures (or cooling rates). The evidence of crossing the parent (δ) boundaries mentioned above is highly suggestive that a massive transformation does occur. It is not surprising that it should be rather slow at temperatures as low as -70°C. As has been shown(1) in alloy systems based on the noble metals, the massive transformation can be very rapid in one system (Cu-Zn) and rather slow in another system (Ag-Cd or Ag-Zn). If a massive transformation does occur, the crystallographic orientation relationship is most likely to be lacking.

E. Transformations Involving the γ, β, and α Phases

Depending upon the cooling rate, the decomposition of γ results in the formation of either β or α. Both transformations, γ to β and γ to α, exhibit isothermal sigmoidal curves(15) that might be considered typical of d-n-a-g reactions. For samples cooled from 260°C, after prior annealing at this temperature for 30 min, Nelson(15) observed that at temperatures above 90°C the $\gamma \rightarrow \beta$ transition proceeded isothermally to completion; in the 90-82°C range the transition is interrupted by the onset of the skip transition $\gamma \rightarrow \alpha$; below 82°C γ decomposes directly to α. In the 82-90°C temperature range an arrest appears between the termination of the $\gamma \rightarrow \beta$ and start of the $\gamma \rightarrow \alpha$ transitions.(15) Evidently, the incubation of α arrests the further formation of β. The TTT curves for the decomposition of γ to β, γ to α, and γ to β to α reported by Nelson(15) are shown in Fig. 19. The curves exhibit a double "C" feature. Maximum rates of transformation for the $\gamma \rightarrow \beta$ transition occur at about 100°C, and for the $\gamma \rightarrow \alpha$ skip transition the maximum rate occurs below -78°C. It seems that at so low a temperature the exact nature of the transformation is open to question. It could be martensitic or perhaps massive. Faiers and White,(71) on gas quenching samples of Pu at a rate of 208 and 280°C/sec from the γ field (270°C), observed that the decomposition of γ occurred in the 67-72°C range and concluded on the basis of Nelson's results(15) that the product formed was α.

Spriet,(14) studying a β-stabilized Pu-3 at.% Zr alloy, states that on the basis of metallography, dilatometry, and thermal analysis the $\gamma \rightarrow \beta$ and $\beta \rightarrow \gamma$ transitions are diffusion controlled. However, except for some metallography on the $\beta \rightarrow \gamma$ transition, which is shown to start with the appearance of γ at grain boundaries, the author does not present any results obtained for this alloy. Selle and Focke,(49) using their criteria related to the behavior of the internal friction and the shear modulus, also conclude that the two transformations are diffusional. Pascard,(62) while suggesting that the transformation was diffusional, noted that the $\gamma \rightarrow \beta$ transition exhibited an extremely diffuse heat evolution and that there was a temperature hysteresis of about 70°C.

The kinetics of the $\gamma \rightarrow \beta$ transformation show an appreciable decrease, with an increase in the prior γ holding temperature.(15,70) Hill(70) attributes this behavior to a reduction in the size and distribution of possible β embryos. In determining equilibrium temperatures, Hill(55) suggests that the β is more easily formed from γ than γ is from β. This conclusion is based on the relative slopes of the plots of temperature vs the logarithm of the inverse of the respective transformation rate. Such plots show that the cooling transition has a greater temperature dependence than the heating transition. For the $\alpha \rightleftarrows \beta$ transitions the reverse behavior is observed. In contrast to the observations for the decomposition of γ to β, the decomposition of γ to α is essentially unaffected by the prior γ heat treatment (holding) temperature.(15) Nelson(15) noted, however, that the rate of formation of α from γ was considerably higher than when it formed from β. Interestingly enough, however, the grain size in samples quenched to -21°C from the β and γ fields, respectively, was quite similar.

Nelson(15) also studied the transitions obtained on heating α or β samples into the γ range, resulting in the reactions $\beta \rightarrow \gamma$ or $\alpha \rightarrow \beta \rightarrow \gamma$. Plutonium samples that had been first "cold treated" (15 min at -23°C) were heated into either the β region (20 min at 180°C) or α region (3 min at 100-110°C) prior to transferring into the γ region for the isothermal studies. Sigmoidal-type curves, typical of three-dimensional growth, were shown for the $\beta \rightarrow \gamma$ transformation. The resulting "C" curves obtained for a TTT plot are shown in Fig. 20. Nelson(15) observes that the characteristics of the kinetics are similar to those obtained for the $\alpha \rightarrow \beta$ transition. Upquenching of the α phase into the γ region resulted in a rapid transition to β in the order of seconds, followed by the $\beta \rightarrow \gamma$ transformation at a rate slightly smaller than that observed by upquenching the β phase. The author, however, states that the difference may be due to a β grain-size effect or to variations in heating time. Specimens were upquenched into oil baths, and the transformation was followed by measuring relative weight changes in situ.

F. Transformations Involving the δ, δ', and ε Phases

Because of the high temperatures it would be expected that the transformations involving the transitions between the δ, δ', and ε phases should be diffusion controlled. The very small temperature hysteresis associated with these transitions also suggests the absence of non-diffusional mechanisms. On the basis of differences in internal friction and shear modulus values across the transition, Selle and Focke(49) claim that the δ' → δ transformation is diffusional but that the reverse δ → δ' may be occurring by shear. This situation seems highly unlikely to us. Karlsson and Pavlick(77) report the results obtained under partially isothermal conditions for a Pu-0.96 wt% Ga alloy heated from the δ to the ε range. They conclude that the reaction occurs by d-n-a-g. Spriet(14) studied the δ ⇄ ε transitions in a δ-stabilized Pu-2 at.% Al alloy using hot-stage microscopy. He describes the microstructural changes observed during the δ → ε transition. Nucleation occurs principally at the grain boundaries, and as the transformation progresses a pronounced surface deformation is obtained. Cooling through the reverse ε → δ transition results in a polygonized structure of δ. The author concludes that both transitions are diffusion-controlled. Faiers and White,(71) with cooling rates varying from 35 to 7000°C/sec, noted for the ε → δ transition a large temperature dependence with cooling rate. A continuous depression in the transition temperature from 460 to 210°C was obtained with an increase in the cooling rate. On the basis of this large dependence on cooling rate the authors preclude the possibility of the presence of athermal martensite. Presumably they imply that at these high rates the ε → δ transition occurs by isothermal martensite. The transition was detected by arrests on thermal cooling curves; the samples were quenched by helium gas. The cooling rates were obtained by the tangent at 270°C. Judging by the similarity in the behavior of the ε → δ transition to that in pure iron,(1) where the γ → α transition temperature is also substantially lowered by the increase in the cooling rate between 1 and 5000 deg/sec, the ε → δ plutonium transformation is probably of the massive type. If this is true a "plateau" temperature might be expected such that further increases in the cooling rate above a certain value would leave the transformation temperature more or less unaltered.

IV. Transformations in Uranium and Some of Its Alloys

Much of the work on phase transformations in U and its alloys was performed in the late fifties and in the mid sixties. Several excellent reviews dealing with various aspects of these studies may be found.(78-82) Uranium, with a melting point of approximately 1132°C,(83) has three allotropes:* γ (775-1132°C)(83) is bcc,(84)

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*As is the case with the whole field of metals and alloys there is no agreed way of designating allotropic forms with symbols that would indicate a possible crystal structure. Thus, the same bcc structure in Pu is designated as ε, in Th as β, and in U and Np as γ.

β (668 to 775°C),(83) is complex tetragonal with 30 atoms per unit cell,(85) and α (below 668°C) is orthorhombic.(86) As determined by x-ray measurements(87) the $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$ transitions are accompanied by volume decreases of 0.70 and 1.12%, respectively. The early studies with the pure metal have shown that neither of the high temperature phases, γ or β, could be retained by quenching. The presence of both diffusional and shear reactions during the $\beta \rightarrow \alpha$ transition has been indicated, but the rapidity in the decomposition of β made it difficult to isolate the various reactions and to identify the temperature regions where the different mechanisms may be operative.

The difficulty of suppressing the $\beta \rightarrow \alpha$ transition so as to retain the β phase of the pure metal at room temperature is illustrated by the results reported by Duwez(88) (Fig. 21). Two thermal arrests were obtained for samples quenched from the γ phase at rates ranging from 5 to 8000°C/sec; the maximum rate lowered the temperature for the $\beta \rightarrow \alpha$ transition to about 360°C. As may be seen from the figure, the transition temperature for both the $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$ reactions varied in a continuous fashion, suggesting that only one mechanism was operative in each case throughout the whole range. In contrast to the results reported by Duwez, Townsend and Burke(89) show a discontinuity in arrest temperature as a function of cooling rate for the $\beta \rightarrow \alpha$ transition (Fig. 22). The authors concluded that for pure U this transition occurs by diffusional growth at slow cooling rates, while above a critical cooling rate of some 65°C/sec the phase change occurs martensitically. This was based on both the microstructures of quenched samples and on the behavior of the M_s temperature on alloying. Extrapolation of M_s values obtained for U-Cr alloys to 0% solute gives a value of about 600°C (Fig. 23), which is close to the value obtained for the unalloyed U by extrapolation of the data in Fig. 22. It may be noted that the data reported by Duwez are reasonably consistent with those shown by these authors.

In the early work(90-92) concerned with unalloyed U, it was generally believed that the $\beta \rightarrow \alpha$ transition for this metal occurred by a martensitic-like mechanism. At that time it was thought that the kinetics for the dilute U alloys could be described in terms of two distinct "C" curves, the lower representing an isothermal shear transformation, the upper a diffusional transformation. White,(93) studying the effect of Cr additions, noted that the "C" curve for the shear transformation shifted to higher temperatures with a decrease in solute concentration, accompanied by a simultaneous narrowing of the gap between the upper and lower transformation curves. Observing that the M_s temperatures could be extrapolated to give values near the equilibrium transition temperature between α and β for zero solute concentration, he concluded that the two "C" curves merged, with the transformation being all martensitic in pure U. These conclusions were drawn in spite of the fact that equiaxed α grains were observed following either slow cooling from β or following an isothermal high temperature transformation. On the other hand, after water quenching a mixed morphology was seen that contained, in addition to the equiaxed grains, some irregular-shaped grain boundaries and acicular constituents.

More recently it has been shown that the upper "C" curve for the $\beta \rightarrow \alpha$ transition in dilute uranium alloys may actually be composed of two "C" curves.(79,94-97) The possibility of temporarily suppressing the $\beta \rightarrow \alpha$ transition on quenching to room temperature by alloying with less than 1 or 2 at.% of a number of elements — Cr,(79,94,98-101) Mo,(97,102,103) Fe,(104) Re,(105-107) Ru(108) — has facilitated the study of the decomposition of β. In general it is observed that in the alloys the $\beta \rightarrow \alpha$ transition can be described in terms of three distinct transformations occurring in each of three temperature ranges depicted by three sets of "C" curves on a TTT diagram. Figure 24(94) is an example of this behavior obtained for a U-0.85 at.% Cr alloy. The regions designated as C_1, C_2, and C_3 are ascribed to diffusional, diffusion-and-shear (bainitic, with solute partitioning), and shear transformations, respectively.

A number of such TTT curves have been reported by Colombié and Foure(95) for very dilute additions (400-1500 ppm each) of Cr, Si, Ge, and Zr, on which are superimposed microstructures related to various isothermal temperatures. Modifications in the decomposition kinetics of β by only minor variations in solute additions are readily seen. Butcher(80) has reviewed some of the published work that attempts to explain the effect of alloying on the suppression of the β decomposition in terms of the atomic diameter of the solutes and their effect on the relative strengths of the α and β phases. Zaimovsky et al.(104) have shown that variations in small amounts of Al, Si, and Fe added to U may cause significant differences in the $\beta \rightarrow \alpha$ transition temperatures for cooling rates between 100 and 400°C/sec. For example, for a cooling rate of 400°C/sec, the addition of less than 0.08 wt% Al + Si + Fe to U caused the critical temperature to drop from 600 to 532°C.

Due to the rapid kinetics obtained for the pure metal, isothermal studies on unalloyed U have been restricted to relatively high transformation temperatures. Contrary to the usual single "C" curve over the high temperature range — 595-655°C — Pickwick and Kitchingman(109) report double "C" curves for a high purity U wire (Fig. 25). The authors claim that the kinetics for the region above 620°C can be described by an Avrami-type expression. With the formation also of relatively smooth grain boundaries the transformation mechanism is undoubtedly d-n-a-g. Although no distinct metallographic transition zone was detected, irregularity of the grain boundaries at lower temperatures, which increased with a drop in temperature, was reported. The transition between the two "C" curves is seen to occur at about 620°C. This temperature falls between the two sets of thermal arrests shown for the pure metal in Fig. 22. It is about 20°C above the value obtained when the M_s values for the U-Cr series (shown in Fig. 23) are extrapolated to 0% Cr. It corresponds closely to the upper temperature limit predicted by Duwez's results,(88) suggesting that the latter results may reflect primarily the lower temperature mechanism. The lower "C" curve observed for the unalloyed metal then would correspond to C_3 of the alloyed uranium. The absence of C_2 for the unalloyed metal is not surprising, for a bainitic reaction should not occur in a pure metal. Thus, it appears quite likely that for the pure metal the $\beta \rightarrow \alpha$ transition can occur by either a diffusional or a martensitic (isothermal) mechanism. With small alloy additions, the reactions become more sluggish, the martensitic transformation is markedly displaced to lower temperature, and an intermediate bainitic reaction is introduced. All three transformations for the $\beta \rightarrow \alpha$ transition are apparently devoid of any athermal component, which means that the martensitic transformations are isothermal and are thermally activated.

For unalloyed U and its dilute alloys, the decomposition of γ proceeds directly to β by a d-n-a-g process. With sufficient alloying — in excess of about 2-5 at.% depending on the solute element — and by moderate quenching, the decomposition of γ readily bypasses the β phase; the γ phase transforms instead to α or to one or more metastable phases that can be described as modifications of α or γ. The formation of the modifications based on α has been attributed to shear mechanisms, while modifications based on γ are supposed to reflect an ordering process. It is not clear, however, to what extent these processes occur by either athermal or isothermal modes, although the ordering reaction must necessarily be a thermally activated one. At elevated temperatures the decomposition of γ clearly occurs by diffusional processes. A large variety of morphologies are developed, depending to some extent on composition but to a major extent on the cooling conditions. Interest has been directed largely to the manner and chronology of the formation of the different phases that are responsible for the observed morphologies rather than to the modes of transformation in each case.

It is known(110) that a low-temperature phase transition occurs in α-uranium in the range of about 42 ± 1°K. This transformation is noncrystallographic in the sense that no change of crystal structure occurs while change takes place in the nature of certain interatomic bonds due to the loss of some electrons from the conduction band as α-U is cooled through the transition temperature. A number of changes and anomalies in various physical properties accompany the transition, and it is believed that the transition involves a second-order transformation and that the low temperature structure is antiferromagnetic.(110,111)

A. The β → α High-Temperature Transformation — Region C_1

In the absence of definitive evidence for the presence of a martensitic-type reaction it is generally accepted that at high temperatures the β → α transformation is diffusional. Donze(112) considered possible evidence in support of either mechanism, diffusional or shear, and concluded that the transformation near the equilibrium temperature cannot be martensitic. The formation of equiaxed α grains, which decrease in size with a decrease in the transformation temperature,(79,94,96,97,108,113-117) can only be explained by a d-n-a-g process. Isothermal kinetics are sigmoidal(47,79,93,109) without any indication of the premature arrest occasionally observed with low-temperature isothermal-shear processes. The fact that single crystals of α can be obtained by cooling a polycrystal from the β phase in a temperature gradient(115,118) precludes the presence of any orientation relationship between the two phases and in our view may suggest a massive transformation, at least under these conditions.

Bar-Or and coworkers(119,120) have described the kinetics for the β → α transition of dilute U-Cr alloys, finding them to be consistent with classical theory for diffusional processes. The effects of Cr additions and of temperature on both nucleation and growth were considered. Degois and Faivre,(121) using Avrami plots, obtained a value of the activation energy on the order of 35 kcal/mole in the 460-650°C temperature range for several U-Cr alloys. A value of 32.6 kcal/mole was reported for a U-1.16 at.% Pt alloy.(96) Since the activation energy is a measure of the temperature dependence in a region where the kinetics decrease with a drop in temperature, those results must necessarily reflect the region below the knee of the upper "C" curve and therefore could, at least in part, refer to the behavior of C_2. These values are consistent with activation energies that may be expected for diffusional processes. In spite of this strong evidence for a diffusional high-temperature β → α transition, a number of investigators contend nevertheless that both the β → α and α → β transitions, even near the equilibrium temperature, must occur by processes analogous to martensite formation.

1. Remnant Textures. Much of the controversy pertaining to both the high-temperature β → α and the reverse α → β transformations evolves around the attempts to explain the return of the same or similar texture originally present in an initially textured α specimen, following an α → β → α sequence of transitions. In other words, the initial texture appears to be somehow "retained" during the α → β → α cycle. This phenomenon has been discussed in some detail in several papers(47,78,122,123) and is frequently referred to as a "memory effect." It is primarily attributed to the retention in the β phase of small α domains or nuclei from the original parent α. A number of studies(47,97,101,112,122,124-127) have been reported that show the influence of time or maximum temperature attained in the β phase during the heating cycle on either

the subsequent $\beta \rightarrow \alpha$ transition kinetics or the microstructure of the α phase. Although arguments have been presented that attempt to ascribe this behavior to a reversible martensitic-type transformation,(91,92,122) by and large the evidence suggests that the "memory effect" is due to the retention of some α on heating into the β field. More controversial is the question of the nature of these α sources. Are the α regions that are present after solution treatment in the β-phase merely regions of untransformed α, or do some special α nuclei or domains form?

Klepfer and Chiotti(92) noted some degree of reversibility (texture retention) following an initial cycling of U through the α-β transition, but they found that on repeated cycling the structure became randomized. These authors attributed the initial retention to the presence of a coherent nucleation and growth process in each of the transitions. However, because of the polygonization and twinning occurring in the α phase, causing fragmentation of the texture, and because of the grain growth occurring in the β phase, causing absorption and destruction of the strained nuclei, the original α texture was soon lost. A similar behavior was noted by Butcher(91) following several quenching cycles from the β field starting with a single crystal. Thermal cycling(92) also caused a decrease in the $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$ transition-start temperatures and increased the temperature at which twinning occurred in the α phase. This so-called "hardening of the lattice" was also attributed to a martensitic transformation. The authors state that the four reactions, $\alpha \rightarrow \beta$, $\beta \rightarrow \alpha$, $\beta \rightarrow \gamma$, and $\gamma \rightarrow \beta$, in the vicinity of the respective equilibrium temperatures all involve initial bursts, then proceed isothermally with a slow approach to an apparent end, which they compare to the slow growth of coherent nuclei.

The presence of α domains after transformation to β, the domains acting as nuclei for the reverse $\beta \rightarrow \alpha$ reaction, has been frequently suggested.(101,112,122-125,127) Donze and Faivre(112,124,127) noted that they were able to regenerate an original single crystal of α after cycling into the β region at low temperatures; but, if cycled to a high temperature within the β phase, subsequent transformation produces a polycrystal. Using a cooling rate of 4°C/hr, they also noted that the $\beta \rightarrow \alpha$ transition temperature decreased with an increase in the prior temperature within the β phase. In agreement with these results Beaudier <u>et al.</u>(125) noted that an increase in the β temperature or in the time at this temperature caused an increase in the incubation period of the following $\beta \rightarrow \alpha$ reaction and a decrease in the transformation rate. A cooling rate of 5°C/hr was used for U and U alloyed with small additions of Cr, Mn, and Mo. Although the retention of textures was not examined, the authors(112,125) believed that the memory effect was not associated with any martensitic reaction but was simply the result of retained α nuclei. As the β temperature is raised the α nuclei are progressively eliminated.

Beaudier et al.,(101) on studying the influence of β temperature over a 100°C range within the β phase, also noted the effect of the β temperature on the subsequent temperature at which the $\beta \rightarrow \alpha$ transition is initiated. Using dilatometry as a criterion for anisotropy, the authors concluded that as the prior β temperature is increased the original orientation in the subsequent α phase was progressively eliminated. However, repeated cycling in the low-temperature β region did not affect the original texture.

Eisenblätter et al.,(123) using a high temperature x-ray diffractometer, measured the intensity from a number of specific diffracting planes for a large number of $\alpha \rightleftarrows \beta$ cycles and concluded that a memory effect does exist not only for α nuclei in β but also for β nuclei in α. They state that the memory effect is reduced by cycling to lower temperatures within the α phase. Erratic variations in their results are obtained, however, which are attributed to lattice misorientations caused by stresses arising from transformation volume changes.

In support of the concept of α domains, Butcher and Baverstock(122) noted, following their $\alpha \rightarrow \beta \rightarrow \alpha$ studies on initially textured α-U, that although the retention of texture decreased with an increase in the extent of the $\alpha \rightarrow \beta$ transformation about one-quarter of the texture was still retained with almost complete transformation to β. This conclusion was based on dilatometric studies, which may be somewhat insensitive to the disappearance of the last traces of the transforming constituent. Assuming that both the $\beta \rightarrow \alpha$ and $\alpha \rightarrow \beta$ transformations are martensitic, the authors propose that the elimination of many of the oriented nuclei formed from the original α could occur by grain growth of the β phase rather than by the $\alpha \rightarrow \beta$ transformation. Their model is illustrated in Fig. 26. It is unfortunate that hot-stage microscopy was not used to confirm this rather interesting possibility. One would expect that the orientation of the α formed in the reverse transformation should be affected more by the distribution of α than by the amount of α.

The (geometric) stability of the α domains or nuclei above the transition temperature is attributed to an array of dislocations at the interface.(78,125) It is difficult to see how such domains are formed in the α and retained in the β and, furthermore, why such a small concentration of domains should exist (one per β grain), as implied by Butcher and Baverstock.(122) Beaudier et al.(125) also proposed that α nuclei are retained and used the model proposed by Dehlinger(128) to support their argument. They further proposed that the differences in results obtained between the pure metal and some dilute alloys could be explained on the basis of an interaction between solute elements and the dislocation networks present at the interfaces of the nuclei. Interaction may tend to stabilize the nuclei and therefore delay the $\beta \rightarrow \alpha$ transformation.

In apparent support of the stabilization effect are the results reported by Beaudier et al.(101) (Fig. 27) for the influence of the initial holding temperature within the β phase on the start of the $\beta \rightarrow \alpha$ transition for unalloyed U and a U-0.6 at.% Cr alloy. As may be seen, a gradual decrease in the start temperature is obtained for the alloy over the entire 100°C range within the β phase that was studied. In contrast, for the pure metal the decrease occurs over a narrow temperature range, about 10-20°C above the $\alpha \rightarrow \beta$ equilibrium temperature. In the latter case it would appear as if a sudden catastrophic dissolution of the α nuclei had occurred. If alloying indeed does stabilize the nuclei, these nuclei should be more readily retained in the alloys during the β treatment. This effect should be reflected in the transformation kinetics and retained textures. Unfortunately, such studies comparing alloyed with unalloyed U were not made. The effect of impurities suggests that stabilized domains may indeed form. We could consider, for example, that as transformation progresses minor impurities are rejected into the moving interface so that isolated "domains" of α then become more and more resistant to further transformation.

McDonell,(126) in opposition to the domain theory, concluded that the retention of preferred orientation was merely the result of some residual untransformed α grains being retained in the β phase and acting as nuclei on cooling. He noted that the retention was smaller in quenched samples than in slowly cooled samples and proposed that this was due to the fact that quenching introduced new random grains of the α phase that compete with the growth of the retained (original) α regions. Barwood and Butcher,(129) in studying by dilatometry the $\alpha \rightarrow \beta$ transformation of textured U, observed that the last stages of the transition were very sluggish but that the reaction is completed only several degrees above the equilibrium temperature. Noting that residual texture after cooling was absent when the prior heating transformation was 100% completed, the authors conclude that the remnant textures after cycling through the $\alpha \rightarrow \beta$ region are not due to the "preservation of α nuclei" but rather to a prior incomplete $\alpha \rightarrow \beta$ transformation. Lehr and Langeron,(115) noting the extent of the irreversibility observed in the dilatometric curves on cycling through the $\alpha \rightleftarrows \beta$ transition, concluded that a crystallographic relationship between these two phases does not exist. On the basis of this and other evidence they concluded that the $\alpha \rightleftarrows \beta$ transitions in U take place by (diffusional) nucleation and growth. They also show that definite textures, however, may be developed on cooling through a temperature gradient. It may be that the observation of remnant structures might, at least in some cases, result from such gradients.

Townsend and Burke(47) performed a comprehensive series of experiments in an attempt to explain the effect of the β temperature prior to quenching on the $\beta \rightarrow \alpha$ transformation kinetics. They were able to show that the effects observed were largely due to the β grain size and only to a minor extent on the temperature itself. On the basis of their results the authors discount the arguments based on the presence of retained α domains.

A variation in β grain size was obtained by changing the cooling rate from the γ region; samples were then quenched from different β temperatures into one of four different temperature regions where isothermal transformation to α took place. The specific effect of grain size on the kinetics was found to be different within each transformation temperature region; this could be explained in terms of the different mechanisms involved for each region. At high temperatures (615-630°C), where the process was diffusion controlled, a decrease in β grain size resulted in an acceleration of the kinetics and was attributed to grain boundary nucleation. Between 500 and 610°C the kinetics were unaffected by grain size, since, as shown by metallographic studies, the nucleation of α was completely random. Between 370 and 500°C a decrease in β grain size caused a small but definite retardation in the kinetics. This was explained on the basis of nucleation within grains and arrest of α platelets at grain boundaries. Below 300°C α forms martensitically, and the latter effect is more pronounced, since the kinetics are primarily reflected by the slow growth rate. The influence of β grain size for the martensitic transformation region is seen in Fig. 28.

Mihajlović *et al.*(97) examined the microstructures of a U-0.45 wt % Mo alloy following quenching (2 to 80°C/sec) from various β temperatures (670-720°C). In contrast to the results reported by other investigators cited above, these authors conclude that the suppression of the β → α transition is greatest when quenched from the lowest β temperatures. On retaining the β phase to room temperature, its subsequent decomposition was slowest following cooling from the higher β temperatures. This again is in contradiction with the observations reported above for the effect of β grain size on the martensitic transformation. The authors propose that the higher β temperature leads to a more disordered state, making it more difficult to suppress the transformation; but, once suppressed, a shear type transformation would be most difficult for the most disordered state. The presence of a possible second-order transition within the β-phase region is suggested by the anomalous heat effect observed on the cooling curves reported by Duwez(88) for unalloyed uranium. Townsend and Burke(47) discuss the possibility for the existence of two modifications of the β phase. Blumenthal,(83) who diligently searched for such an anomaly in his DTA studies on pure U, was unable to detect any.

It was earlier pointed out that the presence of a "memory effect" had suggested that the α → β transition occurs martensitically. Burke and Dixon(78) discuss the α → β transition in some detail and conclude that the transformation is diffusional, except perhaps in the case of very rapid heating of martensitically formed α. They also point out that, although a crystallographic relationship may well exist between α and β, this need not imply the presence of a shear transformation. Widmanstätten structures formed by diffusional processes are well known and result from the minimization of energy by the matching of specific planes between two phases. Bar-Or and Wynblatt,(116) in noting columnar growth of α for the $\beta \rightarrow \alpha$ transformation in a U-0.45 at.% Cr alloy, suggested that remnant structures may be due at least in part to this columnar growth. The growth was attributed to differences in nucleation rate between the surface and interior of a sample.

The kinetics and microstructural observations of specimens isothermally transformed and the possibility of obtaining single crystals of α can only be interpreted for the high-temperature $\beta \rightarrow \alpha$ transformation (region C_1) in terms of a diffusional mechanism. Although we are uncertain as to the significance of the techniques of relative moduli and internal friction measurements for interpretation of transformations, Selle and Focke(49) conclude that both $\alpha \rightleftarrows \beta$ and $\beta \rightleftarrows \gamma$ must be diffusional (at least under slow heating and cooling conditions). The enigma of the "memory effect" therefore is not explicable in terms of a martensitic transformation. The origin of the so-called α nuclei or domains has not been satisfactorily explained. The so-called dissolution of α nuclei may in fact actually be the redistribution of impurities, and thereby affect the reverse $\beta \rightarrow \alpha$ kinetics. The observed grain size effects and the results obtained following completion of the sluggish $\alpha \rightarrow \beta$ transition are strong arguments disqualifying the suggestion of retained nuclei. It would seem that careful studies throughout the entire $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transformation in the vicinity of the $\alpha \rightarrow \beta$ region are needed, perhaps with hot-stage microscopy or electron microscopy.

B. The $\beta \rightarrow \alpha$ Intermediate-Temperature Transformation — Region C_2

Reference to the transformation in region C_2 generally has been made as an adjunct to the "high temperature" and "low temperature" studies. The failure in the early work to recognize the presence of a distinct transformation at the intermediate temperature can undoubtedly be attributed to the inability to separate the upper "C" curve into its two components. For example, White,(93) who obtained TTT curves for a series of U-Cr alloys, noted a feathery appearance in the microstructures for specimens transformed by the "upper C process" yet failed to recognize that this may not be associated solely with a diffusional mechanism. His TTT curves consisted of only upper and lower "C" curves. Jepson et al.(90) obtained $\beta \rightarrow \alpha$ TTT curves for a number of alloys with small amounts of different solute additions. Breaks were obtained in the high temperature region for several of the corresponding "C" curves, but here also the authors failed to recognize the presence of an intermediate transformation. In part, this was due to the fact that the isothermal studies were not always carried out at low enough temperatures to obtain the martensite "C" curves. It was therefore assumed that the martensitic transformation was initiated at these breaks. The authors also observed irregular grain boundaries following transformation of a U-0.5 at.% Cr at 550°C. This corresponds to the region below the knee for the upper "C" curve, which for this alloy did not exhibit a break. The possibility of a bainitic reaction was not considered. Beaudier et al.$^{(101)}$ examined the microstructures for a U-0.6 at.% Cr alloy following partial isothermal exposure at several different temperatures. Using the TTT curves published by White$^{(93)}$ for a similar alloy, the authors concluded that for the upper "C" curve the microstructure developed above the knee is equiaxed, whereas below the knee it is irregular, becoming more and more jagged with a further drop in temperature. Again the possibility of different mechanisms above and below the knee was not examined.

The above metallographic observations suggested to Burke and coworkers$^{(79,94)}$ the possible existence of different mechanisms in different regions of the upper single "C" curves reported$^{(90,93)}$ for U-Cr alloys. In studies of the isothermal $\beta \rightarrow \alpha$ kinetics for U alloys containing 0.5$^{(79)}$ and 0.85$^{(94)}$ at.% Cr by resistivity measurements, discontinuities were obtained at about 500°C in the upper "C" curves that permit its separation into two "C" curves, C_1 and C_2 (see Fig. 24). The likely separation of the upper "C" curves into two curves is now firmly established on the basis of results published for a number of dilute alloys.$^{(94-96)}$ Mihajlović et al.$^{(97)}$ show a TTT diagram for a U-0.45 wt% Mo alloy that is based on continuous cooling from different β temperatures at different cooling rates. Distinct ranges are indicated over which equiaxed or bainitic α phases form.

Kinetics of the transformation of U and its alloys had previously been based largely on dilatometry and metallography. Kitchingman et al.,$^{(96)}$ using both resistivity and dilatometric techniques, showed that, whereas a clear separation into two "C" curves was obtained by resistivity, the same region was represented by an uninterrupted "C" curve when based on dilatometry. This was due to the relative time elapsed in transferring the sample from the β-quench temperature to the isothermal temperatures. Although open-walled silica tubes permitted direct contact of the dilatometer specimen with the isothermal bath, the more massive dilatometer specimens took significantly longer to cool than the resistivity wires; the latter were partially cooled by gas quenching. Thus, the presence of either a single "C" curve or its separation into two upper "C" curves might well be attributed directly to the experimental technique used.

The feathery or acicular-irregular grain boundary microstructures that are typical of the morphology developed as a result of the $\beta \rightarrow \alpha$ transformation in region C_2 have frequently been noted$^{(79,81,90,93,95-97,101,120)}$ (see, for example, Fig. 29). Although White$^{(93)}$ did not recognize the presence of region C_2, he indicated that the isothermal kinetics at intermediate temperatures could be described in the same way as the decomposition of austenite to bainite in steels. For the region below 530°C he obtained an activation energy of about 34 kcal/mole, consistent with a diffusion-controlled reaction. Burke(81) reports an activation energy of 40 kcal/mole for a 0.85 at.% Cr alloy, increasing to 60 kcal/mole at 1% Cr. A value of 32.6 kcal/mole has been reported for the transformation of a U-1.16 at.% Pt alloy in region C_2.(96) Soeno(130) reports values for the activation energy obtained below the knee of the upper "C" curve for dilute additions of Cr, Mn, Si, and V; the values range between 25 and 55 kcal/mole. In contrast to the results above reported by Burke, Soeno reported an increase from 32 to 38 kcal/mole in going from 0.5 to 1.0 at.% Cr.

Kitchingman et al.,(96) plotting hardness vs transformation temperature for a U-1.16 at.% Pt alloy, noted a discontinuity in the hardness values that occurred at a temperature corresponding closely to that where C_1 and C_2 curves intersect. They also noted a discontinuity at about the same temperature for the temperature dependence of change in resistivity accompanying the $\beta \rightarrow \alpha$ transition; the latter effect, however, was minor. Dixon and Burke(79) noted a very similar discontinuity in hardness (Fig. 30) that could also be related to the temperature of intersection or discontinuity on the upper "C" curves for a U-0.5 at.% Cr alloy. The authors suggest that, since the discontinuities on the "C" curves become more apparent with increased amounts of transformation, the difference between C_1 and C_2 mechanisms is more in the growth behavior than in the nucleation behavior. The authors(79,81) also tentatively suggest that the reaction in the region C_2 corresponds to one in which supersaturated α (α') is formed by shear within β with a simultaneous diffusion-controlled precipitation of Cr. Burke(81) also proposes that the precipitation of Cr would then allow plates of α to form martensitically in essentially pure β, with the growth governed by the rate of diffusion of Cr. This behavior would be consistent with the differences in magnitude for the β-grain size sensitivity of the transformations at temperatures corresponding to regions C_2 and C_3.(47) The effect of grain size was attributed to grain boundaries arresting plate growth. Since the growth of plates in region C_2 is influenced primarily by the diffusion and precipitation of Cr out of α, the effect of grain boundaries, and therefore of β-grain size, is relatively less important here than in region C_3. This is supported by the observed influence of the grain size in these two regions. Townsend and Burke,(94) noting that additions of Cr depress C_3 more than C_2, suggest that C_2 is more akin to the known diffusion reaction in C_1 than to the shear reaction in C_3.

Burke,(81) in examining samples partially transformed in region C_2, observed a large number of α-plates or needles randomly nucleated and growing in at least five different directions. On the basis of the traces of these directions he suggested growth on $\{100\}_\beta$ and $\{110\}_\beta$. He noted many similar characteristics between the reactions taking place in regions C_2 and C_1, especially with reference to the microstructure and shape change. The different microstructures obtained in regions C_1, C_2, and C_3(95) are shown in Fig. 31. Kinetically, however, C_2 and C_3 are similar; the two curves overlap. Both produce smooth sigmoidal transformation curves with no evidence of the bursts seen on occasion for region C_3. Burke(81) concludes, at least for dilute U-Cr alloys, that the reaction in region C_2 is of a bainitic type.

The foregoing microstructural and kinetic evidence strongly supports the contention that the reaction in the C_2 range is bainitic — i.e., that it involves both shear and bulk diffusion of the solute. The presence of three types of reactions (a high temperature diffusional, an intermediate temperature bainitic, and a low temperature martensitic reaction) in the dilute uranium alloys is quite analogous to the reactions in steels. However, one might anticipate from the differences observed in the martensitic behavior for the two types of materials that the corresponding bainitic reactions may differ substantially. There is no definitive evidence that the martensitic reaction in uranium alloys is other than isothermal. As will be pointed out in the following section, the kinetic relationship between nucleation and growth during the isothermal martensitic formation in U is quite different from that for the few cases of isothermal martensitic transformation observed in steels. The present status of our knowledge of the bainitic reaction in uranium alloys is probably comparable to the status for this reaction in steels some 30 or more years ago. Whether one or more distinct bainitic reactions occur is not known, although variations in the microstructure would suggest this possibility. Little is known about the crystallography — the transformation shears and lattice correspondences. Very little data on kinetics — especially at different temperatures — are available. And the possibility of a massive transformation without solute partitioning must not be excluded. Much can be done in studying morphological development and the relationship between kinetics and morphology. Various cycling or short-range up-and-down quenching experiments within the C_2 range could be done to isolate or distinguish among the various possible modes of transformation that may be present throughout this range. In short, exploration in the C_2 temperature range offers many exciting possibilities for obtaining a better understanding of the transformation behavior in uranium alloys — an understanding similar to that obtained for other alloy systems.

C. The $\beta \rightarrow \alpha$ Low-Temperature Transformation — Region C_3

Evidence for a shear transformation occurring at the lower temperatures is obtained primarily from metallographic observations(79,81,90,95,97,99-102,104,105,117,130-133) and to a lesser extent inferred from the nature of the isothermal kinetics.(79,93,96,105,131) No definitive evidence exists for any athermal component. The occurrence of a stress- or strain-induced $\beta \rightarrow \alpha$ reaction, even resulting simply from scratching or polishing specimens containing residual β, has been noted frequently.(90,93,100,131) The transformation is also quench-rate sensitive as a result of quenching stresses.(79) Several observations have been attributed to burst or catalytic behavior during transformation, e.g., steps on isothermal plots,(81,93) grouping together of martensitic-like plates,(81,131) isolated heavily transformed regions(105) and jerky growth.(133) Mott and Haines,(100) observing the isothermal behavior microscopically, noted that the transformation was intermittent; each time it was initiated by a sudden burst followed by a decay in growth rate. This behavior was attributed to the buildup of transformation-induced stresses. On relief of these stresses, either by twinning of α or deformation of β, the transformation is again initiated. Such burst behavior has been considered as evidence for possible athermal behavior in a U-Cr alloy.(131)

Figure 32 shows an example of plates (or needles) frequently observed in martensitically formed α. The clusters of small plates are attributed to burst behavior. Slow growth of individual plates has been noted(81,102,131,133) (see Fig. 33). This isothermal growth is considered to be much too slow to be accounted for by normal (bulk) diffusional processes.(105) A shear reaction is also indicated by the homogeneous shearing of scratches by transformation of a pre-scratched surface.(131) In general, one observes that increased solute additions result in a retardation of the transformation kinetics and a shift of the M_s to lower temperatures.(93,94,130) The effect of Cr additions(93) on M_s has previously been noted.* The effect of a number of solute elements on the M_s, according to Soeno,(130) is shown in Fig. 34. The suppression of the $\alpha \rightarrow \beta$ transition to room temperature for small solute additions (less than about $1\frac{1}{2}$ at.%) has been noted on many occasions.(79,94,97,98,100-107,134) However, as White pointed out for chromium additions(93) a reversal in the kinetics may occur if the solubility limit of the β phase were exceeded, since the second phase may provide additional nucleation sites.

1. Kinetics and Stress Effects. Over a limited temperature range within region C_3 the isothermal kinetics, as described by a plot of dilatometer reading vs log time, were shown to flatten out or decrease linearly relatively early during the phase change(93) (Fig. 35). This behavior is to be expected where the stresses that build up due to accommodation strains are of sufficient magnitude to arrest the transformation. Further transformation then can only proceed on relaxation of the stresses. Thus, the kinetics reflect a balance between the introduction and removal of transformation-induced stresses. The difficulty in determining the end of the martensitic transformation was pointed out by White,(93) who noted that the $\beta \rightarrow \alpha$ reaction in several U-Cr alloys, which had apparently

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*The M_s is taken either as the transition temperature between C_2 and C_3 or as the extrapolation of the upper branch of C_2 curve to a temperature at which this branch becomes asymptotic.

stopped at 300°C, again took place on lowering the temperature to 100°C. This points out the importance of the free-energy driving force in overcoming the transformation-induced stresses. In fact, at the lower temperatures the isothermal kinetics are typically sigmoidal.(93) At temperatures above about 325-350°C the transformation stresses are easily relieved and the curves are also sigmoidal.

Dixon and Burke,(79) also working with U-Cr alloys, observed kinetics similar to those reported above by White.(93) Their interpretation, which was based on metallography, x-ray, and resistivity analyses, was quite different from that made by White. The authors concluded that the initial portion of the curve, which started with a sigmoidal behavior, represents a shear transformation of β to supersaturated α (referred to as α'),* while the leveling off corresponds to the decomposition of α' to α and precipitation of a Cr precipitate. The end of the sigmoidal region corresponded to about 60% of the total change in resistivity, yet no residual β could be observed at the end of this stage by x-ray techniques. Evidence for precipitation occurring is also seen in the hardness data. The hardness of the transformed product increased with an increase in transformation temperature; this is attributed to more extensive precipitation at higher temperatures. A sudden drop occurring at about 400°C (see Fig. 36) corresponds to the transition from C_3 to C_2. In view of the strong similarity between curves obtained by two different techniques,(79,93) the different conclusions drawn from such similar curves are difficult to reconcile. In part, the similarity implies that the ratio of the changes of length obtained by dilatometry(93) and resistivity(79) should be for some reason nearly the same, irrespective of whether the cause was transformation or precipitation, a highly unlikely situation.

Holden,(131) in attempting to explain the difference in origin between athermal and isothermal martensitic kinetics, proposed that this difference is due to the relative ease with which the parent phase can plastically deform so as to relieve the transformation-induced stresses. In steels, with the ductile fcc lattice of the parent phase this can easily take place, and a temperature change would be the main criterion for the transformation to proceed. However, for the less ductile β-U, in which slip is limited to the $\{110\}$ $\langle 001 \rangle_\beta$ system,(98) stresses are not readily relieved by the parent β phase. Unfavorably oriented single crystals of β have been shown to be brittle.(98) Thus, in the early stages of transformation, stresses are more readily relieved by twinning in the α plates. Because of plates seen in a quenched U-1 at.% Cr microstructure (5 min after quenching), Holden(131) proposed that some martensite was able to form athermally — at temperatures above 350°C, where α is known to undergo easy slip and where β probably deforms on more slip systems than at low temperatures.

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*Metastable structures are discussed in following sections.

The ductility argument by itself cannot explain the kinetics in terms of a "C" curve, for it is hardly to be expected that as the temperature is lowered below the knee the transformation-induced strain energy would increase at a rate faster than that for the change in free energy. The fact that an appreciable incubation period may be necessary for the isothermal transformation suggests that the nucleation features of this martensitic transformation when compared with an alternative athermal martensitic transformation might differ considerably. It is interesting to note that, where isothermal martensite has been observed for steels, the rate-controlling mechanism is nucleation; the growth of the plates, however, is still sudden as with athermal martensite.(135) Thus, not only must the nucleation features differ between athermal and isothermal martensite but also the controlling mechanisms for the isothermal growth for steels and uranium alloys must differ, for in the latter the growth is slow. The question is still unanswered whether the growth in the uranium transformation is thermally activated because of the necessary adjustments at the interface, because of thermally activated plastic flow (which is needed to relieve stresses in the matrix) or because of the diffusion of impurities ahead of the advancing interface. Lomer(136) proposed that the slow growth is due to the complexity of atomic movements necessary to produce orthorhombic α from complex tetragonal β. This may be a contributing factor, but it certainly cannot account for the intermittent growth of the martensite.(100) Burke(81) attributes the slow growth to the difficulties of accommodating the shape and volume changes by the brittle β phase. Butcher and Rowe(133) considered the transformation as occurring by an initial shearing of the lattice followed by time-dependent heterogeneous atomic readjustments of the sheared, distorted β lattice to form the α lattice. The authors also suggest that the slow growth may be partly due to the relief of stresses in the deformed β, with such relief occurring by polygonization of the β phase. The polygonization would explain the observed spread in orientation of the α phase noted in Laue photographs.(133)

Certainly, thermal activation is implicit where an incubation period is required and growth proceeds isothermally. Kitchingman <u>et al.</u>(96) reported a value for the activation energy of 17.0 kcal/mole for the C_3 transformation in a U-1.16 at.% Pt alloy. Values ranging from 11 to 15 kcal/mole were reported by Burke(80) for a series of U-Cr alloys. Activation energies ranging from 14 to 23 kcal/mole were obtained by Soeno for a series of dilute uranium alloys (U-Cr, U-Fe, U-Mn, U-Si, and U-V).(130) Although the actual shearing mechanism per se may be related to an athermal reaction, its initiation and continuation must depend on activation processes, probably other than those related to normal diffusion processes.

Mihajlović and Mance,(102) studying the microstructure of U-0.45 wt% Mo samples, transformed various amounts at 80°C, room temperature, and -200°C and noted that an acicular or platelet structure was developed initially at all three temperatures, but at the two higher temperatures this gave way to a feathery structure. If a sample with a mixed structure formed at one of the higher temperatures was then cooled to the lower temperature, transformation would then continue by the formation of plates. The authors therefore propose that the mechanisms differ for the two temperature regions (within C_3) in that at the low temperature nucleation and growth is controlled by shear resulting in the formation of only plates, while at the higher temperatures the feathers result from a diffusion-controlled nucleation process, the subsequent growth being shear controlled.

The isothermal growth of individual martensite plates in a U-Cr alloy has been discussed by Burke(81) in considerable detail. As would be expected for a semi-coherent α/β interface, the growth is arrested at a grain boundary. However, typical of other martensitic alloys new plates may be nucleated in a contiguous β grain, probably due to induced stresses at such points. Burke(81) suggested on the basis of the irregular grain structure for the transformed product that the martensite is similar to that observed for Fe-Ni alloys, a structure referred to on occasion as "massive martensite" (a term we suggest should be discarded in view of its possible confusion with massive transformation and instead be replaced by either lath, plate, or bulky martensite).

2. Lattice Correspondence. Possible crystallographic relationships between the α and β crystal structures have been considered by several authors.(92,99,131,133,136,137) The difficulty in predicting a correspondence matrix for the $\beta \rightarrow \alpha$ transition in terms of minimum atomic movement is pointed out by Lomer.(136) This is because of the complex crystal structure of β, which has 30 atoms/cell in contrast to the somewhat simpler structure of α, with 4 atoms/cell. Lomer attacked the problem by ignoring the atomic positions and instead considering the transformation of a set of lattice vectors from one structure to that of the other such that each of the vectors in one set is an integral number of the corresponding vectors of the second set. In addition, the volumes defined by the two sets of corresponding vectors contain equal number of atoms and that the transformation strain is not too large.

Of the many different correspondences possible, four were considered acceptable on the basis of sufficiently small transformation strains. Although the proposed correspondences are in reasonable agreement with observations, the author considers that it is unlikely that the transformation occurs martensitically (in the classical sense), for the homogeneous shear places only 1 atom in 30 (or 60 for 2 cells) into its correct position. Instead, he proposes that the adjustments from β to α positions spread progressively through the crystal as a coherent growth of α at expense of β. More recently, Crocker and Ross(137) again examined the problem and pointed out that many other correspondences with comparatively small strains exist. For the various correspondences considered, again only 1 atom in 30 moves directly to its correct final site. The authors then suggest that the subsequent shuffling required of the remaining atoms may be the controlling factor in deciding which correspondences are likely to arise in practice.

Holden(131) and Butcher and Rowe(99,133) have reported for U-Cr alloys that the habit plane is approximately of the $\{321\}_\beta$ type. The latter authors have also found evidence for the $\{441\}_\beta$ as being another habit plane for the $\beta \rightarrow \alpha$ transformation. The correspondence lattices are reported by Butcher and Rowe(133) as $(001)_\alpha \parallel (\bar{8}17)_\beta$, $(010)_\alpha \parallel (\bar{1}2\bar{3}4)_\beta$, $\{021\}_\alpha \parallel \{410\}_\beta$, and approximately $\{001\}_\alpha \parallel \{410\}_\beta$. Holden reported the orientation relationship as $(001)_\alpha \parallel (101)_\beta$. In general, the crystallographic relationship (by x-ray methods) was difficult to establish conclusively because of various experimental problems — lack of intensity, highly strained α, too fine a grain size in α, and especially the duplicity in the superposition of the low-index planes, making their separation difficult.

D. The Decomposition and Transformations of the High-Temperature γ Phase

Although numerous studies have been reported on the decomposition and transformation of γ in uranium alloys, relatively little work deals directly with the $\gamma \rightarrow \beta$ transition. Compared with the large influence caused by alloying on the $\beta \rightarrow \alpha$ transition, small quantities of alloying elements, up to about 1 or 2 at.%, apparently have relatively little effect on the $\beta \rightleftarrows \gamma$ high-temperature allotropic change. The work reported by Duwez(88) on the influence of the cooling rate in depressing the $\gamma \rightarrow \beta$ transition temperature for pure U has already been cited (Fig. 21). Collot and Faivre(138) showed a similar moderate effect for two U-Nb alloys (2.5 and 5.0 at.% Nb), the effect being greatest with the higher Nb alloy. An increase in the cooling rate from 1 to about 2000°C/min caused the transition temperature to decrease by about 80 and 115°C for the lower and higher Nb contents, respectively. Several studies have shown, however, that the $\gamma \rightleftarrows \beta$ transitions in pure U may be suppressed altogether, with the transition occurring directly between γ and α and between α and γ. Such suppression follows, for example, with a dispersion of BeO or UO_2 powders in pure U.(139,140) By decreasing the amount of oxide the $\gamma \rightleftarrows \beta$ transitions were reintroduced. The authors attributed the suppression or elimination of the $\gamma \rightarrow \beta$ transition to the difficulty of nucleating the β structure. Somewhat similar results were obtained with a mixture of U and graphite powders,(141) in which case both the $\alpha \rightleftarrows \beta$ and $\beta \rightleftarrows \alpha$ transitions were affected. Östberg et al.(142) studied the decomposition kinetics of γ in the β field for several U materials containing about 2000 ppm of impurities, mainly Fe and Al. They were concerned, however, with the precipitation of second-phase particles such as UAl_2, rather than with the $\gamma \rightarrow \beta$ transition.

It is apparent, on reviewing the literature, that very little effort has been directed toward studying the nature of the $\gamma \rightarrow \beta$ transition in U metal. This is undoubtedly due to the absence of any major technological problems incidental to the $\gamma \rightleftarrows \beta$ change. One would suppose that the transition occurs by a d-n-a-g process. However, with the addition of a number of alloying elements in excess of about 2-5 at.% and with only moderate cooling rates, the decomposition of γ becomes quite involved, offering many possible alternatives; the β phase frequently does not appear at all. Although the extension of the β-phase field in the phase diagrams is limited to additions of about 2-3 at.% of solute for the alloys investigated, the β constituent is present in equilibrium with an additional intermediate phase over a relatively wide range of solute concentrations for most of these alloys — about 33 at.% each for Ru, Re, and Ti, and about 63 at.% for Zr. The elements Mo and Nb introduce a $\beta \rightarrow (\alpha + \gamma)$ eutectoid reaction, with the two-phase $(\beta + \gamma)$ region extending to about 12 at.% of solute. Thus, the β phase appears in many of the alloys investigated, following slow cooling or high-temperature isothermal holding. The absence of β following faster cooling conditions or following isothermal transformations at the lower temperatures must be the result of the more favorable kinetics for the decomposition of γ into alternative metastable structures.

1. Structures Obtained on Continuous Cooling. We shall first consider the observations made under nonisothermal conditions. The transformation studies on the U-base alloys have been concerned largely with the nature of the decomposition products of γ obtained by continuous cooling, their morphology, and the sequence of formation of the different crystal structures. The formation of several different crystal structures and the variety of morphologies obtained can be the consequence of both the cooling rate(103,106-108,134,143-150) and composition.(103,106-108,134,143, 145-154) The initial γ grain size and the initial quench temperature are also important.(103,106,107,155) Numerous x-ray studies have been made on the various metastable phases obtained with additions of Mo,(103,134,143,147,148,150-152) Nb,(143,149,153) Ru,(108,154) Zr,(144,145,156) Ti,(157-159) and Re.(106,107,160) In addition to identifying the structures, much of the work was concerned with attempts to understand the effect of alloying on changes in lattice dimensions and the influence of such changes on the composition limits over which these structures are stable. Studies have also been made on the orientation relationship that may exist between γ and the different metastable phases.(143,147,151,156,161) The metastable structures formed are modifications of the orthorhombic α and bcc γ structures. Lehmann and Hills(146) have proposed a scheme for labeling metastable phases that, in part, takes into account specific morphologies by the use of subscripts, e.g., "a" for acicular, "b" for banded, and "n" for nucleation and growth, the latter probably implying diffusional processes. Evidently, the scheme has not been followed vigorously, as the subscripts are frequently omitted.

Many similarities exist between the different alloy systems that have been investigated. We feel that the subject may best be introduced with reference first to only one of the many comprehensive studies that have been reported. Jackson and Larsen(107) examined the nature of the products of decomposition of γ obtained on quenching a series of U-Re alloys from the γ region. Figure 37 lists the different structures obtained as influenced by Re content, severity of quench, and the γ quench temperature. The α' and α" designations refer to a modification of the α phase. On moderate alloying the b lattice parameter of the orthorhombic structure decreases, with corresponding slight expansions of the a and c axes — this modification is denoted as α'. With higher alloying the angle γ between the a and b axes departs from 90°C, resulting in a monoclinic structure, α". The γ° structure is believed to be a tetragonal-ordered phase derived from the bcc γ structure.

Considering a 7-at.%-Re alloy cooled from 975°C, it may be noted from Fig. 37 that the slower quench yields α" while the more rapid quench develops α'; for a 9-at.% alloy the phases observed are retained γ and α" for the two quenching rates, respectively. This suggested that whereas an increase in Re content results in a correspondingly greater distortion in the (martensitic) product from the α structure, an increase in cooling rate reverses this trend. The degree of the departure from the α structure is considered to be a function of the stiffening of the lattice against shear by alloying, while the approach to the α structure is attributed to enhancement of the shear by quenching stresses.(107,147,150,153) Thus, for low solute contents and moderate quenching rates, shear can occur readily to produce the α' structure. As the alloy content is increased shear is increasingly restricted and the critical amount of shear required to produce the α' structure is not realized. Instead, the α" structure is developed with the orthorhombic angle departing more and more from 90° with increased alloying. At sufficiently high solute contents the modified γ (γ°) or retained γ structures are obtained. With increased severity in quenching, the critical shear can be realized more readily and the transitions in crystal structures are shifted to higher solute concentrations. Tangri(150) proposed that some optimum value of the ratio of the quenching stress to lattice stiffening is required to generate any one of these martensitic phases. This value is referred to as a stress/stiffening ratio.

Observations that more or less fit this scheme of phase changes are seen in U-Re,(106,107) U-Mo,(134,143,147,157) U-Nb,(143,147,149,153) U-Zr,(145) and U-Ru(108,154) systems. However, the α" structure is absent in the U-Ru and U-Zr alloys. It has been proposed that the presence of the α" structure is related to the influence of the solute atom size(143,153) and to a critical decrease in the b parameter value.(143) The absence of α" in the

U-Ru and U-Zr systems is suggested as being due to very limited,(108,153,154) or completely lacking(153) compressibility in the direction of the b parameter in these two systems, respectively. The non-uniform change in the a, b, and c parameters of the orthorhombic α-U structure with alloying is considered to be due to the substitution of "elliptical-shaped" U atoms by "spherical" solute atoms.(143)

An example of the influence of quenching rate on morphology is seen in Fig. 38 for the 9-at.%-Re alloy, which shows (a) untransformed γ and (b) α'' structures, referred to, respectively, in (a) and (b) of Fig. 37. Figure 39 shows an α' banded structure, while a Widmanstätten morphology showing "crosshatch" α'' is seen in Fig. 40. So-called flag and granular structures of α are seen in Figs. 41 and 42. A banded acicular structure containing γ^o is seen in Fig. 43. It would be incorrect to say that these are typical morphologies, for many variations in microstructure are known, some of which may be the result of a martensitic transformation and some which may not. By far the most common morphologies are those associated with some form of banding, as seen for alloys of U-Zr,(144,145,156) U-Mo,(82,103,134,146-148,152,162,163) U-Ti,(82,158) U-Ru,(108,154) U-Re,(106,107) and U-Nb.(82,143,164) In general, a transition from acicular and granular structures to banded and Widmanstätten structures occurs with increase in solute concentration. Different families of bands are commonly observed together, which are probably in many cases related to sequences of transitions or to different periods of a given transition. Coarse bands have been attributed to mechanical twinning of the γ phase, while the fine bands and the Widmanstätten structure are most likely due to lenticular plates arising from the shear transformation of γ to either α' or α''.(107) Butcher(162) has considered in some detail the deformation of the bcc γ by twinning, proposing the usual {112} twin mode and suggesting that one of the metastable γ phases twins on the {122} planes.

The α' structure is present in various morphologies at the lower solute concentrations — in granular, acicular, flag type, irregular-shaped boundaries, as well as in bands — and it may have formed either by a d-n-a-g or a shear process or both. In addition, as pointed out by Hills et al.(103) for U-Mo alloys, the α' formed from β has a different appearance than that formed from γ, the latter having, in general, a more "regular" shape. The long individual needles or plates that frequently are seen following a $\beta \rightarrow \alpha$ shear transformation are not observed in α formed directly from γ. These long needles have grown uninterrupted during the isothermal $\beta \rightarrow \alpha$ phase change. The absence of such long needles in α formed from γ could be due either to the interference with the twin boundaries or to a much higher nucleation-to-growth rate in the γ phase.

Crystallographic relationships between γ and its products have been proposed by several investigators.(143,147,151,156) Jackson and Larson(107) note that the tendency towards metastable transition phases is usually most pronounced for the bcc → hcp transitions. The α-U structure bears a striking likeness to the hcp structure except that successive layers of atoms in the basal plane may be considered to be skewed back and forth in the $\langle 010 \rangle$ directions. The addition of alloying elements (such as Re) that decrease the b/a ratio, makes the α lattice more like the hcp lattice. Hatt,(156) by considering α-U as a distorted hcp structure and using as an analogy the bcc → hcp transformation in Zr, proposed that the $\gamma \rightarrow \alpha'$ transformation for U-Zr alloys occurs by shear on $\{112\}_\gamma$ planes in $\langle 111 \rangle_\gamma$ directions accompanied by glide on alternate planes of $\{110\}_\gamma$ in $\langle 110 \rangle_\gamma$ directions. He further proposes that the bands observed are twin related, resulting from transformation of γ along crystallographically equivalent paths. To generate α' or α'' only one set of $\{112\}_\gamma$ planes is required. On the basis of this proposal, Tangri and Williams(147) present a model showing that below a critical amount of shear the α' structure cannot be generated and instead the α'' structure results. Below still a lower critical value the α'' cannot form and instead γ° forms with very limited shear on two $\{112\}_\gamma$ planes. The $\{112\}_\gamma \langle 111 \rangle_\gamma$ transformation shear mode is also proposed for the formation of metastable phases in U-Nb alloys(143) and U-Mo alloys.(151)

The decomposition of γ through several progressive stages on quenching from the γ region has been suggested by several authors.(107,147,151,156,165) Stewart and Williams(151) determined the atomic positions of the α'' structure for U-10 at.% Mo samples water quenched from the γ field. On the basis of a reverse $\alpha'' \rightarrow \gamma^\circ$ transition that resulted from reheating a quenched sample, they conclude that for this alloy the decomposition of γ proceeds by $\gamma \rightarrow \gamma^\circ \rightarrow \alpha''$. Hatt,(156) referring to unpublished work, states that for Mo additions the α'' structure forms by two successive martensitic transformations. Support for the transition occurring by progressive stages is also seen in the results reported by Yakel(165) for a U-16.60 at.% Nb-5.64 at.% Zr alloy in which a transition structure γ^s was obtained on water quenching from the γ region. On reheating to within the range of 150 to 350°C the γ^s gradually changed to γ°. Both transitions are described in terms of atomic shifts, and thus the γ° may be different from the ordered γ° described for the binary alloys. The author suggests that "the two transitions represent successive steps by which the alloy lowers its free energy and approaches a structural arrangement more like that of the equilibrium α phase." The decomposition of β to α through an intermediate phase referred as $\beta\alpha$ was reported for a U-1.2 wt% Re alloy.(106)

The decomposition of γ through successive stages is not an unreasonable occurrence considering the similarity between γ and γ° and between α, α', and α''. For the U-Zr and U-Ru alloys the α'' stage would be bypassed (or exist temporarily in a highly metastable condition). The presence of transition stages is consistent with the observed dependence of the resulting structures on the cooling rate. We had previously noted that for certain given compositions an increase in quenching rate results in the presence of γ^o, α'', and α', respectively. Since the quenching stresses would be expected to increase as the temperature is lowered during a quench, a sequence such as $\gamma^o \rightarrow \alpha'' \rightarrow \alpha'$ may be expected to occur during a suitable quench in a sample of a composition that possesses an appropriate stress/stiffening ratio. Such behavior should be detectable by some simple experimental techniques involving resistivity, dilatometry, thermal cooling curves, and some means of measuring elastic and anelastic behavior.

In contrast to the above arguments, Tangri *et al.*(154) propose that the formation of α' and its coexistence with γ^o for a U-10 at.% Re alloy results from the depletion of Ru in the residual γ as the γ^o phase grows. The Ru-depleted regions thus become more susceptible to shear and transform directly to α'. The formation of phases as a result of enrichment or depletion is commonly proposed to explain the structures obtained following isothermal decomposition at elevated temperatures.

Reference to the decomposition of γ occurring by a shear (martensitic) mechanism on rapid cooling from the γ field has frequently been made.(106-108,134,143-145,148-152,154,156,158,161,162,164,166) However, it is not clear whether the martensite products form athermally or isothermally; and, in fact, we are not aware of any efforts made to clarify this question. Much of the effort in the nonisothermal studies has been directed toward "speculating" on the chronology of transitions that might lead to the observed morphologies obtained on continuous cooling.(107,108,134,145,147,161) In many of the studies hardness measurements were made that aided in the interpretation of the metallographic and structural results.

Hills *et al.*(145) discuss in considerable detail the possible modes of transformation (and precipitation) that could produce the various morphologies, structures, and the resulting hardness of quenched U-Zr rods. Composition varied from 2.5 to 50 at.% Zr. Rods were end-quenched into mercury, giving a wide range of cooling rates. Both diffusional and shear mechanisms were considered to be operative and competitive, their presence depending on quench rates and composition. Somewhat similar end-quench studies were made on other systems.(91,108,134) Although these studies provide considerable insight with respect to the relationship of structure and morphology to composition and thermal parameters, considerably less effort was apparently directed toward understanding the transformation mechanisms per se than for the $\beta \rightarrow \alpha$ transition of U and its dilute alloys. In addition to morphology and structure studies, much of the work was concerned with understanding of the influence of solute concentration on the unit-cell angle of the γ phase or the three lattice parameters *a*, *b*, and *c* of the α' and α'' structures,(143,147,151-154,158) and on the *c*/*a* ratio of

γ^o.(143,147,151,153) The possibility of a $\gamma \rightarrow \beta$ massive transformation on the basis of the presence of smooth boundaries of contiguous β grains was also suggested.(108)

2. Isothermal Changes. A number of studies have been reported on the isothermal decomposition of γ for various uranium binary and ternary alloys containing Mo, Nb, Zr, Pu, [illegible], Ti, and Pt.(82,97,142,144,148,149,155,163,167-177) A review of some of the early work is given by Rough and Bauer.(175) Interest was directed primarily toward the identification of phases, the kinetics of their formation and the chronology and morphology of their development, and to a lesser extent to an understanding of the transformation mechanisms per se. As may be seen the direction taken in these studies are not too dissimilar from that reported for the nonisothermal work; and, although much information was presented on morphologies and their development, little additional knowledge was gained regarding transformation mechanisms. We feel that it is not the mission of this paper to pursue the subject of morphologies in any detail if such information does not lead to additional insight into the mechanisms involved. We shall, therefore, only point out some of the general trends observed and mention briefly any information that will be of more pertinent interest to the objective of this paper.

Interpretation of the isothermal behavior was often based on metallography of samples quenched to room temperature, following various isothermal treatments. This was frequently supplemented by resistivity and dilatometric studies, as well as room temperature hardness, density, and x-ray measurements. Typically, following treatment at the higher temperature ranges (above about 600-650°C), first β (its presence depending on the alloy and solute concentration) and then α precipitate from the γ in a lamellar-like morphology somewhat resembling coarse pearlite in steels. It is commonly suggested that the precipitation occurs coherently along specific crystallographic planes of the γ matrix. Orientation relationships have been observed between the parent and product phases in these d-n-a-g reactions. The nucleation is almost invariably suggested as occurring at the γ grain boundaries. For the higher solute concentrations, the precipitation of α (and β) results in an enrichment in solute concentration in the residual γ, which, at least for the Mo-U base alloys, then converts to the ordered γ' state, the latter forming within the α. Widmanstätten as well as cellular morphologies are also observed.

With holding at intermediate temperatures (about 500-600°C), the lamellae of α are finer and may tend towards an acicular appearance. A cellular morphology has also been observed. In some cases fine α grains are nucleated. For the low solute concentrations irregular-shaped α grains form with a dispersion of spheroidal particles of γ, suggestive of a bainitic reaction. In other cases the $\alpha + \gamma$ lamellar formation changes to a different morphology with time. The intermediate-temperature range for some alloys may best be described in terms of two or three regions, different morphologies developing not only as a function of temperature but also as a function of the holding time.

For temperatures below about 400-500°C the morphologies are quite similar to those seen for the quenched alloys. Shear transformations are frequently proposed for the low-temperature transformations, in which the formation of α', α'', and/or γ^o are observed.

A number of TTT curves have been reported.(144,148,163,167-170, 172-175,178) These are frequently divided into different regions according to the various phases present and based primarily on changes in properties. Figure 44 shows an example of such a TTT curve obtained for a U-6 at.% Mo alloy.(163) Figure 45 illustrates the varied behavior that can be obtained for the initiation of a transformation, depending on the technique used. Very few of the curves show M_S lines.(144,148,163,170) These are shown as being horizontal (although indicated as being uncertain) and imply that the martensitic transformations occur athermally.

We recognize the complexity involved with the presence of the many changes that occur on the decomposition of γ in U alloys. Thus, it may be difficult to isolate individual phase changes for the purpose of better understanding the kinetics and the atomistic mechanisms involved. Yet, this must be done, possibly with careful appropriate choices of composition. Even with the present alloys it would seem that information could be obtained as to the kinetic nature of each martensitic transformation. Subzero-temperature studies, as well as upquenching to temperatures not too far above room temperature (avoiding precipitation), should provide useful kinetic data. A knowledge of the effects of concurrent stress and strain during the decomposition process should also be of value, especially when related to the concept of the stress/concentration ratio and the composition limits of the α', α'', and γ^o structures. Studies at subzero temperatures should provide additional information on the possibility of progressive changes involving γ^o, α'', and α'. It is clear that much remains to be done on clarifying the status of transformation mechanism in uranium-base alloys involving the decomposition of the γ phase.

V. Allotropic Transformations in Thorium, Neptunium, and Americium

The allotropic transition in thorium, between the α (fcc) and β (bcc) structures, occurs at high temperatures (1360-1400° ± 25°C) and is therefore most likely of the d-n-a-g type. Studies involving additions of alloying elements show that of the elements that have been investigated(179-181) — In, Si, Al, Ce, Hf, U, Zr, Nb, Ta, V, C and Y — only C and Y increase the transformation temperature. Since the stability of the high temperature β phase is undoubtedly in a good measure due to the contribution derived from the vibrational entropy associated with elastic anisotropy of the bcc structure, it might be expected that elements that would stiffen the lattice due to the size effect might push the transition temperature up on alloying, thereby reducing the temperature range of stability of the bcc phase. Additions of most of the rare-earth metals raise the transformation temperature initially, again apparently due to the size effect.(182) Other explanations in terms of electronic factors have been proposed, but there is no good way of deciding which particular factor is predominant. We are not aware that the nature of the allotropic transformation process in thorium has been studied in any detail.

Neptunium can exist in three allotropic forms,(6) which have the orthorhombic (α, below 280 ± 5°C), tetragonal (β, 280-577 ± 5°C), and most likely bcc (γ, 577-637 ± 2°C) structures. Neptunium is the first in the series of transuranic elements and only recently has become available in sufficient quantity and purity to allow investigation of its physical properties, including allotropic transformations. The most striking feature of the α phase microstructure obtained by quenching from the β phase to -80°C is the presence of fine twinning;(183) it has been suggested that this twinning is the result of a martensitic transformation taking place during the β → α change. It is not known whether the quench to -80°C significantly depresses the transformation temperature below the equilibrium value. The nature of the β → α transition occurring at near-equilibrium temperature (~280°C) is less certain,(183) but it may be expected that the volume change of approximately 2.85% should oppose the transformation kinetics more effectively when the driving force is reduced. The calculated volume change during the β → γ transition is 3.25%, but the transformation temperature is near 600°C, where strain effects should be less important.

Observations made by Nelson and Bowman(183) suggest that the progress of the α → β transition is independent of time, and this is also true of the β → α transition, which shows very little hysteresis. This suggests a diffusionless, martensitic type of transformation that, unlike the α → β transition in Pu, is not thermally activated.

Selle and Rechtien(6) have measured the internal friction of Np from room temperature to 595°C using a low-frequency inverted-torsion pendulum. On the basis of the criteria that have been mentioned earlier they concluded that the β → α and α → β transformations involve both shear and diffusional components but that basically the most likely nature of these reactions is of the isothermal shear type, a conclusion that is in disagreement with the time-independent feature noted by Nelson and Bowman.

The changes in the dynamic internal friction associated with the β → γ and γ → β transitions(6) are shown in Fig. 46. As may be seen, the general shape and the respective values of internal friction before and after the transformation are different on heating and on cooling, and the authors conclude that the transformation on heating is diffusional and that on cooling martensitic. In view of the tentative nature of the internal friction approach it is perhaps too early to consider these conclusions as final.

Americium is still very scarce; only a few studies have been made on this metal and purities ranged from 99.5 to 99.9%. According to McWhan et al.,(184) stable Am at room temperature is dhcp, which is the same structure as that of the rare-earth elements La, Pr, and Nd. This appears to confirm the fact that Am is the first actinide to be properly considered as a rare-earth element. The above authors reported evidence that Am transforms from dhcp to fcc structure between 600 and 700°C and then melts at 994°C. Stephens et al.(185) add more support to the conclusion that Am is like a rare-earth metal and point out that one of the properties that all rare earths seem to exhibit is that they are close-packed at room temperature but transform to the bcc structure before melting. Accordingly, they propose that the sequence of structures in Am on heating is most likely dhcp → fcc → bcc, and they suggest that the fcc → bcc transition takes place at about 1072°C and melting occurs at 1173°C. The values are based on data obtained from pressure studies and extrapolated to 1 atm. Thermal studies by Wade and Wolf(186) indicate a solid-state transition at 1079°C with melting occurring at 1176°C, the two values being reasonably close to those reported by Stephens et al. No studies of solid-state transformations appear to have been reported for this metal as yet.

VI. Some Concluding Remarks

It is perhaps well to conclude that it is probably incorrect and unwise to approach the field of solid-state transformations, particularly the transformations of the allotropic kind, with the expectation that each particular transition may be associated with a definite process, diffusional or martensitic, and that one of the general aims of research in this area might be to discover the nature of this process in each case. Evidence has been mounting for a number of years that most transformations that do not involve a major change of composition may occur in a number of ways depending on conditions, the foremost of which is the rate of the temperature change. The transformations in the actinide metals illustrate the above point very well, and this is perhaps the reason for the diversity of opinion and the confusion sometimes evident in the literature.

For Pu and U, the situation seems less clear in the former metal. In Pu, the available evidence strongly suggests that both the $\beta \rightarrow \alpha$ and $\delta \rightarrow \gamma$ transitions are mainly martensitic during rapid cooling. On slow cooling the latter transition most likely occurs by a d-n-a-g process. The transformation mechanisms of the $\beta \rightarrow \alpha$ transition on slow cooling remain highly controversial. The $\delta \rightarrow \alpha$ skip transition probably occurs by a martensitic transformation. The remaining transitions all appear to take place by diffusional processes, although the possible presence of a shear mechanism in several of these transitions is still in dispute, especially for the $\alpha \rightarrow \beta$ transition. Furthermore, it is not to be unexpected that under very rapid heating or cooling massive transformations might occur for some of these transitions. Reference to this possibility was made for the $\delta \rightarrow \alpha$ and $\epsilon \rightarrow \delta$ transitions.

Based on the majority of established criteria, the low-temperature $\beta \rightarrow \alpha$ transformation in U and its dilute alloys is unquestionably martensitic. On slow cooling, however, the $\beta \rightarrow \alpha$ transition occurs primarily by d-n-a-g processes. At intermediate cooling conditions both d-n-a-g and shear processes (bainite formation) occur. The remaining transitions, $\beta \rightarrow \alpha$ and $\gamma \rightleftarrows \beta$, are shown to take place by d-n-a-g processes under all conditions that have been studied. Considerable controversy, however, exists regarding the origin of remnant structures, which suggests the presence of a crystallographic relationship between the $\alpha \rightleftarrows \beta$ transitions at high temperatures. Such relationships need not imply the presence of either shear or diffusional mechanisms. For the higher alloy contents, the decomposition and transformation of γ may become quite complex, varying considerably with composition and cooling rate. Both d-n-a-g and martensitic processes are observed, with the frequent formation of metastable (transitional) structures.

Of special interest is the apparent similarity in the martensitic transformation of the $\beta \rightarrow \alpha$ transitions in U and Pu; changes between different pairs of crystal forms are involved for each metal. The transformation in both systems occurs isothermally. In U (and probably also in Pu) the isothermal growth kinetics, i.e., slow growth, are different from those observed for many other isothermal martensites in which, although nucleation is slow, the growth is rapid. Finally, while it may be desirable to ascertain which particular process may be occurring in a particular case, most transformations appear to be able to occur by an alternative process if the conditions are sufficiently altered. This is an important conclusion with profound consequences for the present and future technology.

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References

1. Massalski, T. B., "Massive Transformations," in *ASM Symposium on Solid State Transformations, Cleveland, Ohio, 1970* (in press).

2. Perspectives in Materials Research, L. Himmel, J. J. Harwood and W. J. Harris, Eds. (Office of Naval Research, Washington, D. C. 1963).

3. Avrami, M., *J. Chem. Phys.* *8*, 212 (1940).

4. Johnson, W. A., and Mehl, R. F., *Trans. Met. Soc. AIME* *135*, 416 (1939).

5. Selle, J. E., *An Internal Friction Study of Allotropic Transformations*, Ph. D. Thesis, University of Cincinnati, Cincinnati, Ohio, 1967.

6. Selle, J. E., and Rechtien, J. J., *J. Nucl. Mater.* *31*, 203 (1969).

7. Liptai, R. G., Dunegan, H. L., and Tatro, C. A., *Acoustic Emissions Generated During Phase Transformations in Metals and Alloys*, Lawrence Radiation Laboratory, Livermore, California, Rept. UCRL-50525 (1968).

8. Davy, L. G. T., Faiers, M. E., and White, J. S., *J. Nucl. Mater.* *22*, 197 (1967).

9. Rosen, M., Lloyd, L. T., and Petersen, R. G., "The $\beta \rightarrow \alpha$ Phase Transformation in High Purity Plutonium," in *Plutonium 1965*, A. E. Kay and M. B. Waldron, Eds. (Chapman and Hall, London, 1967), pp. 18-38.

10. Nelson, R. D., and Thomas, I. D., "Transformation Kinetics of Plutonium", in *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958*, Vol. 6, pp. 170-173.

11. Loasby, R. G., and Lowe, J. N., "Kinetics of the $\beta \rightarrow \alpha$ Transformation in Plutonium" in *Plutonium 1960*, E. Grison, W. B. H. Lord, and R. D. Fowler Eds., (Cleaver-Hume Press, Ltd., London, 1960), pp. 3-16.

12. Nelson, R. D., *J. Nucl. Mater.* *23*, 238 (1967).

13. Nelson, R. D., Trans. Am. Soc. Metals 51, 677 (1959).

14. Spriet, B., "Study of Allotropic Transformation of Plutonium," in Plutonium 1965, A. E. Kay and M. B. Waldron, Eds. (Chapman and Hall, London, 1967), pp. 88-117.

15. Nelson, R. D., "A Study of the Transformation Kinetics of Alpha, Beta, and Gamma Plutonium," in Extractive and Physical Metallurgy of Plutonium and Its Alloys, W. D. Wilkinson, Ed. (Interscience Publishers, New York, 1960), pp. 215-230.

16. Hanson, I. G., and Pavlick, J.E., J. Nucl. Mater. 27, 100 (1968).

17. Davy, L. G. T., and White, J. S., J. Nucl. Mater. 12, 221 (1964).

18. Galerne, R., and Spriet, B., Compt. Rend. 260, 3961 (1965).

19. Nachtrieb, N. H., Weil, J. A., Catalona, E., and Lawson, A. W., J. Chem. Phys. 20, 1189 (1952).

20. Nelson, R. D., and Shyne, J. C., J. Nucl. Mater. 19, 345 (1966).

21. Knapp, A., and Dehlinger, M., Acta Met. 4, 289 (1956).

22. Spriet, B., J. Nucl. Mater. 16, 59 (1965).

23. White, J. S., and Owen, W. S., J. Iron Steel Inst. 195, 79 (1960).

24. Spriet, B, J. Nucl. Mater. 19, 348 (1966).

25. Nelson, R. D., Discussion, Session One, in Plutonium 1960, E. Grison, W. B. H. Lord, and R. D. Fowler, Eds. (Cleaver-Hume Press, Ltd., London, 1960), pp. 30-32.

26. Spriet, B., Mem. Sci. Rev. Met. 63, 563 (1966).

27. Ekbom, L., and Bogegard, S., "The $\beta \rightarrow \alpha$ Transformation in Small Specimens of Plutonium Metal," in Plutonium 1965, A. E. Kay and M. B. Waldron, Eds. (Chapman and Hall, London, 1967), pp. 49-53.

28. Liptai, R. G., and Friddle, R. J., J. Nucl. Mater. 20, 48 (1966).

29. Spriet, B., J. Nucl. Mater. 13, 13 (1964).

30. Nelson, R. D., Bierlein, T. K., and Bowman, F. E., The Beta-Alpha and Alpha-Beta Transformations in Plutonium Under Applied Stresses, Pacific Northwest Laboratory, Richland, Washington, Rept. BNWL-33 (1965).

31. Liptai, R. G., and Friddle, R. J., *J. Less-Common Metals 10*, 290 (1966).

32. Anderson, J. W., Gilmore, R. R., and Maraman, W. J.,"Studies on the Equilibrium Temperature for the $\alpha - \beta$ Transformation," *Plutonium 1965*, A. E. Kay and M. B. Waldron, Eds. (Chapman and Hall, London, 1967), pp. 39-48.

33. Nelson, R. D., and Shyne, J. C., *Trans. Met. Soc. AIME 236*, 1725 (1966).

34. Nelson, R. D., Bowman, F. E., and Bierlein, T. K., "Transformation and Deformation in Plutonium" in *Plutonium 1965*, A. E. Kay and M. B. Waldron, Eds. (Chapman and Hall, London, 1967), pp. 1-17.

35. Liptai, R. G., and Friddle, R. J., *J. Nucl. Mater. 24*, 316 (1967).

36. Elliott, R. O., Olsen, C. E., and Bronisz, S. E., *Phys. Rev. Letters 12*, 276 (1964).

37. Nelson, R. D., *Transformation Rates of Plastically Deformed Plutonium*, Pacific Northwest Laboratory, Richland, Washington, Rept. BNWL-203 (1966).

38. Bronisz, S. E., and Tate, R. E., *Trans. Met. Soc. AIME 233*, 1396 (1965).

39. Spriet, B., *J. Nucl. Mater. 15*, 113 (1965).

40. Ayers, J. D., *The β to α Massive Transformations in Ag-Zn, Ag-Cd, and Cu-Zn Alloys*, Ph. D. Thesis, Carnegie Mellon University, Pittsburgh, Pa., 1970.

41. Averbach, B. L., "The Effect of Plastic Deformation on Solid Reactions, Part I - Diffusion Reactions," in *Cold Working of Metals* (American Society for Metals, Cleveland, Ohio, 1949), pp. 262-289.

42. Patel, J. R., and Cohen, M., *Acta Met. 1*, 531 (1953).

43. Kaufman, L., and Cohen, M., "Thermodynamics and Kinetics of Martensite Transformations," in *Progress in Metal Physics*, B. Chalmers and R. King, Eds. (Pergamon Press, N. Y., 1958), Vol. 7, pp. 165-245.

44. Averbach, B. L., Kulin, S. A., and Cohen, M., "The Effect of Plastic Deformation on Solid Reactions, Part II - The Effect of Applied Stress and Strain on the Martensite Reaction," in *Cold Working of Metals* (American Society for Metals, Cleveland, Ohio, 1949), pp. 290-319.

45. Kurdymov, G. V., Maksimova, A. I., Nikonorova, A. I., Pavlenko, Z. D., and Yampolskii, A. M., *Phys. Metals Met.* **6**, 85 (1958).

46. Nelson, R. D., Pacific Northwest Laboratory, Richland, Washington, private communication.

47. Townsend, R. D., and Burke, J., *J. Nucl. Mater.* **17**, 215 (1965).

48. Nelson, R. D., and Bowman, F. E., *Trans. Met. Soc. AIME* **245**, 967 (1969).

49. Selle, J. E., and Focke, A. E., *J. Nucl. Mater.* **33**, 149 (1969).

50. Fiedler, H. E., Averbach, B. L., and Cohen, M., *Trans. Am. Soc. Metals* **47**, 267 (1955).

51. Bodine, E. G., Farkas, M. S. and Pardue, W. M., *J. Nucl. Mater.* **15**, 184 (1965).

52. Faiers, M. E., Loasby, R. G., Ward, B. J., Orme, J. T., and Spicer, B. R., "Transformation Kinetics of the α - β and δ - α Transitions in Alloyed Plutonium," in *Plutonium 1965*, A. E. Kay and M. B. Waldron, Eds. (Chapman and Hall, London, 1967), pp. 64-87.

53. *Plutonium Handbook*, O. J. Wick, Ed. (Gordon and Breach, Science Publishers, New York, 1967), Vol. 1, p. 37.

54. Loasby, R. G., "Discussion, Session 2," in *Plutonium 1965*, A. E. Kay and M. B. Waldron, Eds. (Chapman and Hall, London, 1967), pp. 144-145.

55. Hill, J. D., *Nature* **186**, 304 (1960).

56. Burgers, W. G., and Groen, L. J., *Discussions Faraday Soc.* **23**, 183 (1957).

57. Spriet, B., *J. Nucl. Mater.* **19**, 343 (1966).

58. Selle, J. E., and Etter, D. E., *J. Nucl. Mater.* **19**, 341 (1966).

59. Liptai, R. G., *J. Nucl. Mater.* **22**, 117 (1967).

60. Harbur, D. R., Anderson, J. W. and Maraman, W. J., *J. Nucl. Mater.* **30**, 289 (1969).

61. Ludemann, W. D., Lawrence Radiation Laboratory, Livermore, California, private communication.

62. Pascard, R., *Acta Met.* **1**, 305 (1959).

63. Pascard, R., "Etude par Dilatometrie de la Tranformation $\delta \rightarrow \gamma$ du Plutonium Pur," in *Plutonium 1960*, E. Grison, W. B. H. Lord, and R. D. Fowler, Eds. (Cleaver-Hume Press, Ltd., London, 1960), pp. 16-25.

64. Abramson, R., Boucher, R., Fabre, R., and Monti, H., "Some Properties of Plutonium and Aluminum-Plutonium Alloy," in *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958*, Vol. 6, pp. 174-178.

65. Taylor, J. M., "Discussion Session One," *Plutonium 1960*, E. Grison, W. B. H. Lord, and R. D. Fowler, Eds. (Cleaver-Hume Press, Ltd., London, 1960), pp. 32-37.

66. Lee, J. A., and Mardon, P. G., "Some Physical Properties of Plutonium Metal Studied at Harwell," in *The Metal Plutonium*, A. S. Coffinberry and W. N. Miner, Eds. (University of Chicago Press, Chicago, 1961), pp. 133-151.

67. Hocheid, B., and Tanon, A., *Acta Met.* *13*, 144 (1965).

68. Hocheid, B., Tanon, A. and Miard, F., *Mem. Sci. Rev. Met.* *62*, 683 (1965).

69. Hill, J. D., "Discussion, Session One," in *Plutonium 1960*, E. Grison, W. B. H. Lord, R. D. Fowler, Eds. (Cleaver-Hume Press, Ltd., London, 1960), pp. 37-38.

70. Hill, J. D., *J. Less-Common Metals* *4*, 376 (1962).

71. Faiers, M. E., and White, J. S., *J. Nucl. Mater.* *13*, 125 (1964).

72. Elliott, R. O., Olsen, C. E., and Louie, J., *J. Phys. Chem. Solids* *23*, 1029 (1962).

73. Hambling, P. G., Spicer, B. R., White, J. S., *J. Nucl. Mater.* *17*, 172 (1965).

74. Elliott, R. O., and Gschneidner, Jr., K. A., "Behavior of Some Delta-Stabilized Plutonium Alloys at High Pressures," in *Physical Metallurgy of Plutonium and its Alloys*, W. D. Wilkinson, Ed. (Interscience Publishers, New York, 1960), pp. 243-262.

75. Lomer, W. M., *Solid State Commun.* *1*, 96 (1963).

76. Ward, B. J., "Discussion, Session 2," in *Plutonium 1965*, A. E. Kay and M. B. Waldron, Eds. (Chapman and Hall, London, 1967). pp. 145.

77. Karlsson, R. H., and Pavlick, J. E., *J. Nucl. Mater. 19*, 198 (1966).

78. Burke, J., and Dixon, P. H., *J. Nucl. Mater. 7*, 38 (1962).

79. Dixon, P. H., and Burke, J., "A Resistometric Study of the Beta → Alpha Phase Change in a Uranium-1/2% Chromium Alloy," in *Proceedings of a Symposium, Uranium and Graphite* (The Institute of Metals, London, 1962), pp. 9-16.

80. Butcher, B. R., "Grain Size and Preferred Orientation of Uranium," in *Proceedings of a Symposium, Uranium and Graphite* (The Institute of Metals, London, 1962), pp. 1-7.

81. Burke, J., "Martensite and Bainite Transformations in Uranium," in *Physical Properties of Martensite and Bainite*, Iron and Steel Institute, England, Special Report 93 (1965), pp. 83-89.

82. Butcher, B. R., and Holden, A. N., "The Kinetics and Crystallography of the Transformations between the Primary Phases of Uranium and Its Dilute Alloys," in *Progress in Nuclear Energy*, M. Finniston and J. P. Howe, Eds., *Series, V. Vol. 2*, "Metallurgy in Fuels" (Pergamon Press, New York, 1959), pp. 419-429.

83. Blumenthal, B., *J. Nucl. Mater. 2*, 23 (1960).

84. Wilson, A. S., and Rundle, R. E., *Acta Crystallog. 2*, 126 (1949).

85. Tucker, Jr., C. W., *Acta Crystallog. 4*, 425 (1951).

86. Jacob, C. W., and Warren, B. E., *J. Am. Chem. Soc. 59*, 2588 (1937).

87. Chiotti, P., Klepfer, H. H., and White, R. W., *Trans. Am. Soc. Metals 51*, 772 (1959).

88. Duwez, P., *J. Appl. Phys. 24*, 152 (1953).

89. Townsend, R. D., and Burke, J., *J. Nucl. Mater. 17*, 279 (1965).

90. Jepson, M. D., Kehoe, R. B., Nichols, R. W., and Slattery, G. F., "Transformation Behavior of some Dilute Uranium Alloys," in *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958*, Vol. 6, pp. 42-54.

91. Butcher, B. R., *J. Nucl. Energy 4*, 273 (1957).

92. Klepfer, H. H., and Chiotti, P., *Characteristics of the Solid State Transformations in Uranium*, Ames Laboratory, Iowa State College, Ames, Iowa, Rept. ISC-893 (1957).

93. White, Jr., D. W., J. Metals, Trans. AIME 203, 1221 (1955).

94. Townsend, R. D., and Burke, J., Nature 205, 794 (1965).

95. Colombié, M., and Foure, M., Mem. Sci. Rev. Met. 63, 253 (1966).

96. Kitchingman, W. J., Pickwick, K. M., Brown, I. G., and Edwards, R. J., J. Nucl. Mater. 18, 219 (1966).

97. Mihajlović, A., Kostić, M., and Tepvac, P., J. Nucl. Mater. 31, 107 (1969).

98. Holden, A. N., Acta Crystallog. 5, 182 (1952).

99. Butcher, B. R., and Rowe, A. H., Nature 172, 817 (1953).

100. Mott, B. W., and Haines, H. R., Rev. Met. 51, 614 (1954).

101. Beaudier, J., Cabane, G., and Mouturat, P., Mem. Sci. Rev. Met. 58, 176 (1961).

102. Mihajlović, A., and Mance, A., J. Nucl. Mater. 32, 357 (1969).

103. Hills, R. F., Howlett, B. W., and Butcher, B. R., J. Less-Common Metals 5, 369 (1963).

104. Zaimovsky, A. S., Sergeev, G. Y., Titova, V. V., Levitsky, B. M., and Sokursky, Y. N., "Influence of the Structure and Properties of Uranium on Its Behavior Under Irradiation," in Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Vol. 5, pp.566-573.

105. Jackson, R. J., and Larsen, W. L., J. Nucl. Mater. 21, 277 (1967).

106. Jackson, R. J., Williams, D. E., and Larsen, W. L., J. Less-Common Metals 5, 443 (1963).

107. Jackson, R. J., and Larsen, W. L., J. Nucl. Mater. 21, 263 (1967).

108. Hills, R. F., Howlett, B. W., and Butcher, B. R., J. Nucl. Mater. 16, 109 (1965).

109. Pickwick, K. M., and Kitchingman, W. J., J. Nucl. Mater. 19, 109 (1966).

110. Fisher, E. S., and McSkimin, H. J., Phys. Rev. 124, 67 (1961).

111. Meaden, G. T., and Sze, N. H., Cryogenics 8, 396 (1968).

112. Donze, G., J. Nucl. Mater. 5, 150 (1962).

113. Cahn, R. W., Acta Met. 1, 176 (1953).

114. Lacombe, P., and Calais, D., "The Growth of Large Perfect Crystals of Uranium by Cold Working and Annealing Polygonized Crystals Obtained by Beta-Alpha Phase Transformation," in Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Vol. 6, pp. 3-13.

115. Lehr, P., and Langeron, J. P., Rev. Met. 55, 829 (1958).

116. Bar-Or, A., and Wynblatt, P., J. Inst. Metals 92, 183 (1963).

117. Wynblatt, P., and Bar-Or, A., J. Nucl. Mater. 12, 237 (1964).

118. Lehr, P., Compt. Rend. 241, 1043 (1955).

119. Bar-Or, A., Wynblatt, P., and Hirsch, G., Nature 199, 585 (1963).

120. Bar-Or, A., Wynblatt, P., and Hirsch, G., Trans. Met. Soc. AIME 233, 1100 (1965).

121. Degois, M., and Faivre, R., Compt. Rend. 256, 3685 (1963).

122. Butcher, B. R. and Baverstock, D., J. Nucl. Mater. 3, 30 (1961).

123. Eisenblätter, J., Haase, G., and Granzer, F., J. Nucl. Mater. 21, 53 (1967).

124. Donze, G., and Faivre, R., Compt. Rend. 246, 3619 (1958).

125. Beaudier, J., Donze, G., and Cabane, G., J. Nucl. Mater. 4, 325 (1961).

126. McDonell, W. R., Nucl. Sci. Eng. 12, 325 (1962).

127. Donze, G., and Faivre, R., Mem. Sci. Rev. Met. 57, 16 (1960).

128. Dehlinger, U., Z. Metallk. 51, 353 (1960).

129. Harwood, I. F. and Butcher, B. R., J. Nucl. Mater. 8, 232 (1963).

130. Soeno, K., J. At. Energy Soc. Japan 5, 754 (1963).

131. Holden, A. N., Acta Met. 1, 617 (1953).

132. Soeno, K., *Nippon Genshiryoku Gakkaishi* *5*, 665 (1963).

133. Butcher, B. R. and Rowe, A. H., "The Crystallography of the $\beta \rightarrow \alpha$ Phase Transformation in Uranium-1.4 Atomic Per Cent Chromium Alloy," in *The Mechanism of Phase Transformations in Metals*, Monograph and Report Series No. 18 (The Institute of Metals, London, 1956), pp. 229-242.

134. Hills, R. F., and Butcher, B. R., *J. Less-Common Metals* *3*, 155 (1961).

135. Jawson, M. A., "The Nucleation Problem in Martensite," in *The Mechanism of Phase Transformations in Metals*, Monograph and Report Series No. 18 (The Institute of Metals, London, 1956), pp. 173-185.

136. Lomer, W. M., "The $\beta \rightarrow \alpha$ Transformation in Uranium-1.4 Atomic Per Cent Chromium Alloy," in *The Mechanism of Phase Transformations in Metals*, Monograph and Report Series No. 18, (The Institute of Metals, London, 1956), pp. 243-252.

137. Crocker, A. G., and Ross, N. D. H., "The Crystallography of Martensitic Transformations in Uranium and Its Alloys," in *The Mechanisms of Phase Transformations in Crystalline Solids*, Rept. 33 (Institute of Metals, London, 1969), pp. 176-180.

138. Collet, C., and Faivre, R., *Compt. Rend.* *256*, 151 (1963).

139. Besson, J., Blum, P. L., and Laugier J., *J. Nucl. Mater.* *16*, 74 (1965).

140. Besson, J., Blum, P. L., Guinet, P., and Laugier, J., *Compt. Rend.* 259, 3012 (1964).

141. Gregoire, P., Azou, P., and Bastien, P., *Compt. Rend.* *257*, 2481 (1963).

142. Östberg, G., Haglund, B. O., Lehtinen, B., and Storm, L., *J. Microscopie* *5*, 21 (1966).

143. Anagonostidis, M., Colombié, M., and Monti, H., *J. Nucl. Mater.* *11*, 67 (1964).

144. Virot, A., *J. Nucl. Mater.* *5*, 109 (1962).

145. Hills, R. F., Butcher, B. R., and Howlett, B. W., *J. Nucl. Mater.* 16, 25 (1965).

146. Lehmann, J., and Hills, R. F., *J. Nucl. Mater.* *2*, 261 (1960).

147. Tangri, K., and Williams, G. I., *J. Nucl. Mater. 4*, 226 (1961).

148. Lehmann, J., *Rev. Met. 56*, 457 (1959).

149. Bastelli, M. R., D'Amato, C., Giacchetti, G. C., Granata, S., Renzoni, R., Saraceno, F. S., Wilson, T. B., Piatti, G., and Thielsen, R., "Fundamental Metallurgical Studies for the Improvement of Metallic Uranium Fuel Elements," in *A/Conference 28/P/864*, May 1964, pp. 190-196.

150. Tangri, K., *Mem. Sci. Rev. Met. 58*, 469 (1961).

151. Stewart, D., and Williams, G. I., *J. Nucl. Mater. 20*, 262 (1966).

152. Lehmann, J., *J. Nucl. Mater. 4*, 218 (1961).

153. Tangri, K., and Chaudhuri, D. K., *J. Nucl. Mater. 15*, 278 (1965).

154. Tangri, K., Chaudhuri, D. K., and Rao, C. N., *J. Nucl. Mater. 15*, 288 (1965).

155. Lehmann, J., and Decours, J., *J. Nucl. Mater. 12*, 70 (1964).

156. Hatt, B. A., *J. Nucl. Mater. 19*, 133 (1966).

157. Anagnostidis, M., Buschwitz, R., and Colombié, M., *Mem. Sci. Rev. Met. 63*, 163 (1966).

158. Douglas, D. L., *Trans. Am. Soc. Metals 53*, 307 (1961).

159. Harding, A., Waldron, M., and Knight, C., *Transformations in Uranium Alloys with High Solute Solubility in the B.C.C. Gamma Phase. Part 1. Preliminary Observations on the "Banded Structures" Produced by Non-Equilibrium Transformations in Uranium Alloys*, Harwell (UK) Rept. AERE M/R 2673A (1958).

160. Hatt, B. A., and Crook, G. B., Fulmer Research Institute, Rept. R. 53 (1957).

161. Hatt, B. A., and Roberts, J. A., Fulmer Research Institute, Rept. R 114/9 (1960).

162. Butcher, B. R., and Hatt, B. A., *J. Nucl. Mater. 11*, 163 (1964).

163. Howlett, B. W., Eycott, A. J., Kang, I. K., and West, D. R. F., *J. Nucl. Mater. 9*, 143 (1963).

164. Mihajlović, A., and Mance, A., *J. Nucl. Mater. 26*, 267 (1968).

165. Yakel, H. L., *J. Nucl. Mater. 33*, 286 (1969).

166. Pfeil, P. C. L., *J. Inst. Metals 77*, 553 (1950).

167. Van Thyne, R. J., and McPherson, D. J., Trans. Am. Soc. Metals 49, 576 (1957).

168. Van Thyne, R. J., and McPherson, D. J., Trans. Am. Soc. Metals 49, 598 (1957).

169. Kramer, D., and Rhodes, C. G., Trans. Met. Soc. AIME 224, 1015 (1962).

170. Djurić, B., Bilten Instituta Za Nuklearne Nauke Boris Kidrič 16, 150 (1965).

171. Savage, H., J. Nucl. Mater. 25, 241 (1968).

172. Repas, P. E., Goodenow, R. H., and Hehemann, R. F., Trans. Am. Soc. Metals 57, 150 (1964).

173. Mikailoff, H., Métaux (Corrosion-Ind.) 35, 89 (1960).

174. Bellot, J., Dosiere, P., and Henry, J. M., Métaux (Corrosion Ind.) 33, 343 (1958).

175. Rough, F. A., and Bauer, A. A., "Kinetics of Transformations of Gamma-Phase Uranium Alloys," in Progress in Nuclear Energy, H. M. Finniston and J. P. Howe, Eds., Series V, Vol. 2, "Metallurgy in Fuels" (Pergamon Press, New York, 1959), pp. 460-474.

176. Lehmann, J., and Azam, N., J. Nucl. Mater. 10, 73 (1963).

177. Justusson, W. M., J. Nucl. Mater. 4, 37 (1961).

178. Mardon, P. G., "Discussion, Second Session," in Plutonium 1960, E. Grison, W. B. H. Lord, and R. D. Fowler, Eds. (Cleaver-Hume Press, Ltd., 1961), pp. 387-388.

179. Bannister, G. H., and Thomson, J. R., J. Nucl. Mater. 12, 16 (1964).

180. Eash, D. T., and Carlson, O. N., Trans. Am. Soc. Metals 52, 1097 (1960).

181. Chiotti, P., J. Electrochem. Soc. 101, 567 (1954).

182. Uy, J. C., and Burr, A. A., J. Less-Common Metals 11, 149 (1966).

183. Nelson, R. D., and Bowman, F. E., The Physical Metallurgy of Neptunium (Battelle Memorial Institute, Pacific Northwest Laboratory, Richland, Washington, 1968).

184. McWhan, D. B., Cunningham, B. B., and Wallman, J. C., *J. Inorg. Nucl. Chem.* *24*, 1025 (1962).

185. Stephens, D. R., Stromberg, H. D., and Lilley, E. M., *J. Phys. Chem. Solids* *29*, 815 (1968).

186. Wade, W. Z., and Wolf, T., *J. Inorg. Nucl. Chem.* *29*, 2577 (1967).

FIGURE CAPTIONS

1. Dilatometric curves for electrorefined Pu using heating and cooling rates of 4.5°C/min.

2. Isothermal reaction curves of the $\beta \rightarrow \alpha$ transformation in Pu showing the fraction transformed as a function of time (based on weight change in fluid.(13)

3. Time-temperature transformation curves of the $\beta \rightarrow \alpha$ transformations of Pu (based on weight change in fluid).(13)

4. Avrami plots of the $\beta \rightarrow \alpha$ transformation in Pu (based on fluid displacement).(33)

5. Schematic TTT curves proposed for diffusional and martensitic reactions of the $\alpha \rightleftarrows \beta$ transformations in Pu.(22)

6. TTT curves for the $\beta \rightarrow \alpha$ transformation of (a) Pu-0.23 at.% Ti and (b) Pu-1.05 at.% Ti (based on resistivity).(17)

7. TTT curves for the $\beta \rightarrow \alpha$ transformation of Pu with different purities for 50% transformation (based on resistivity).(14)

8. Fraction of weight increase, after cold treating at -21°C and re-weighing at 26°C, of Pu samples that had undergone an apparent complete $\beta \rightarrow \alpha$ transformation at indicated isothermal temperatures. W_i, W_f, and W_g refer to weights in fluid in initial condition, after isothermal treatment, and after cold treatment, respectively.(13)

9. Schematic diagram showing the orientation of the plates of columnar grains following the $\beta \rightarrow \alpha$ transformation in Pu under different stress conditions.(33)

10. Effect of β plastic deformation at 140°C on the Pu $\beta \rightarrow \alpha$ transformation at 80°C.(33)

11. Effect of applied uniaxial stress on the temperature for the start of the $\beta \rightarrow \alpha$ transformation in Pu, while cooling at 2°C/hr. The effects predicted separately by the volume change and the applied stress are denoted by V and S, respectively, and are shown to add to give the observed values indicated by O. The subscripts T and C refer to tensile and compressive stresses, respectively (based on density).(33)

12. Effect of applied uniaxial stress on the temperature for the start of the $\alpha \rightarrow \beta$ transformation in Pu while heating at 2°C/hr (based on density).(33)

13. DTA tracing showing the DTA anomaly preceding the $\alpha \rightarrow \beta$ transition in Pu on heating at a rate of approximately 1°C/min.(61)

14. DTA tracing showing the DTA anomaly preceding the α → β transition in Pu on heating at a rate of 3°C/min.(58)

15. A dilatometric heating and cooling cycle of Pu in the γ and δ regions.(63)

16. The effect of compressive strain applied at various temperatures on the room temperature density of a metastable δ-phase, Pu-2.2 at.% Ce alloy.(73)

17. TTT curves for δ → α transformation of a Pu-0.85 at.% Ga alloy (based on dilatometry and density).(52)

18. Density changes as a result of the δ → α transformation on thermal cycling of Pu-0.85 at.% Ga alloy between (a) -80 and 25°C, (b) -80 and 100°C, and (c) 25 and 100°C for 250 cycles, cooled to -80°C, then continued cycling between 25 and 100°C for 50 additional cycles.(52)

19. TTT curves of the γ → β → α transformation in Pu (based on fluid displacement).(15)

20. TTT curves of the β → γ transformation in Pu (based on fluid displacement).(15)

21. Effect of cooling rate on the allotropic transformation temperatures of U (based on thermal arrests).(88)

22. Effect of cooling rate on the β → α transformation temperature of U (based on thermal arrests).(89)

23. Effect of chromium content on the M_s of the β → α transformation in dilute U-Cr alloys.(89)

24. TTT diagram for the β → α transformations in U-0.85 at.% Cr (based on resistivity).(94)

25. TTT diagram for the β → α transformations in high-purity U (based on resistivity).(109)

26. Schematic representation of the loss of preferred orientation in α as a result of cycling to different temperatures in the β region. Hatching indicates β; arrows represent orientation of grains; dotted lines represent original α nuclei.(122)

27. The effect of the temperature of heating in the β field on the β → α transformation temperature in U and a U-0.6 at.% Cr alloy (based on metallography). Specimens cooled at 5°C/hr to different temperatures and then water quenched.(101)

28. Effect of β quenching temperature on the TTT diagram for U-0.85 wt% Cr alloy below 300°C (based on resistivity).(47)

29. Microstructure of α-U in U-0.5 at.% Cr formed by isothermal transformations at 450°C (region C_2). Polarized light.(81)

30. Effect of $\beta \rightarrow \alpha$ transformation temperature in regions C_1 and C_2 on the variation of microhardness (relative values) for a U-0.5 at.% Cr alloy.(79)

31. TTT curves of the $\beta \rightarrow \alpha$ transformations and microstructures for a dilute U-Cr-Si-Zr alloy. TTT curves based on dilatometry and metallography. Specimens quenched from 900°C.(95)

32. Microstructure of a dilute U-Cr sample quenched from the β field. Shows clusters of martensite needles suggestive of a burst phenomenon. Polarized light.(131)

33. Microstructures showing stages of growth of martensite plates in a dilute U-Cr crystal undergoing a $\beta \rightarrow \alpha$ transformation at room temperature. (a) 2:50 p.m., (b) 3:05 p.m., (c) 3:20 p.m., and (d) 3:55 p.m. Polarized light.(131)

34. Effect of alloying elements on the $\beta \rightarrow \alpha$ M_s temperature.(130)

35. Transformation-time curve representing typical isothermal $\beta \rightarrow \alpha$ transformation kinetics for dilute U-Cr alloys at intermediate temperatures of region C_3.(93)

36. Effect of $\beta \rightarrow \alpha$ transformation temperature in region C_3 (and lower limit of C_2) on the variation of microhardness (relative values) for a U-0.5 at.% Cr alloy.(79)

37. Effect of cooling rate and quenching temperature in the γ region on the crystal structure produced in the U-Re system. Vacuum quench given as ~10°C/sec; water quench ~1000°C/sec.(107)

38. Comparison of microstructures of a U-9 at.% Re alloy water quenched and vacuum quenched from 975°C: (a) vacuum quenched showing clean equiaxed grains of γ structure, (b) water quenched showing single-phase, martensite-like α'' structure. Polarized light.(107)

39. Banded microstructure obtained by water quenching a U-6 at.% Re alloy from 850°C showing α' consisting of coarse twins and fine martensite plates. Polarized light.(107)

40. Widmanstätten-like morphology obtained by vacuum quenching a U-8 at.% Re alloy from 975°C. View shows "crosshatch" α'' martensite plates. Polarized light.(107)

41. Fine "granular" α structure formed on "moderate" cooling a U-4.17 at.% Mo alloy from the γ field. Polarized light.(47)

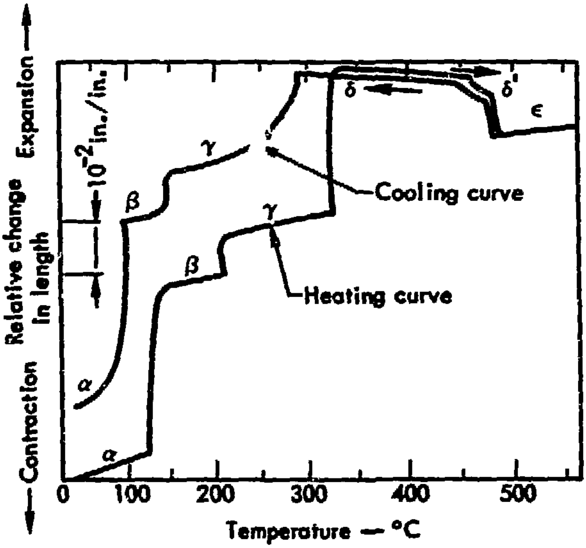
42. "Flag" α structure formed on "slow" cooling a U-4.17 at.% Mo alloy from the γ-field. Polarized light.(47)

43. Microstructure of a U-17.3 at.% Nb alloy water quenched from 1000°C. Shows γ^{o} bands. Anodic oxidation. Polarized light.(143)

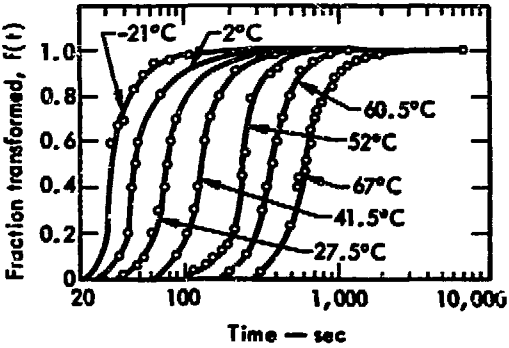
44. TTT diagram for the decomposition of γ in a U-6 at.% Mo alloy (based on dilatometry and hardness).(163)

45. TTT curves for a U-5.4 wt% Mo alloy illustrating the differences in time obtained for the start of the transformation (decomposition of γ) as determined by various techniques.(168)

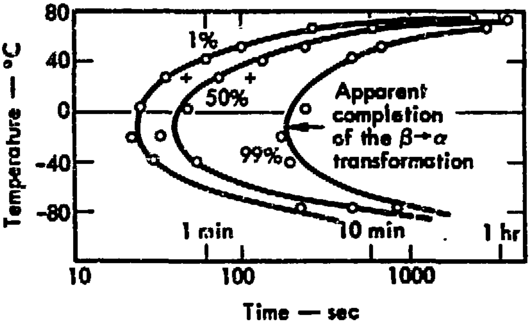
46. Dynamic internal friction vs temperature cruves of the $\gamma \rightarrow \beta$ and $\beta \rightarrow \gamma$ transformations. Heating and cooling rates of approximately 0.5°C/min.(6)



Goldberg - Fig. 1



Goldberg - Fig. 2



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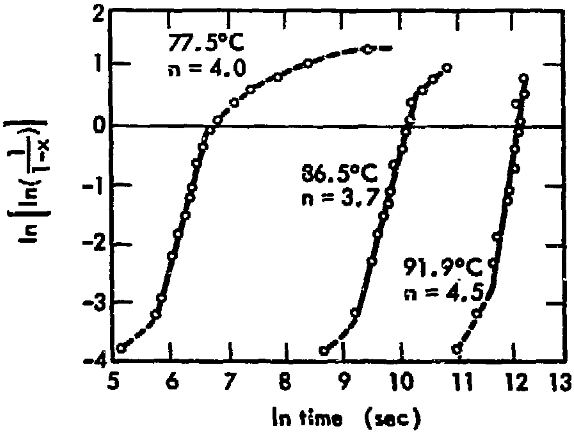

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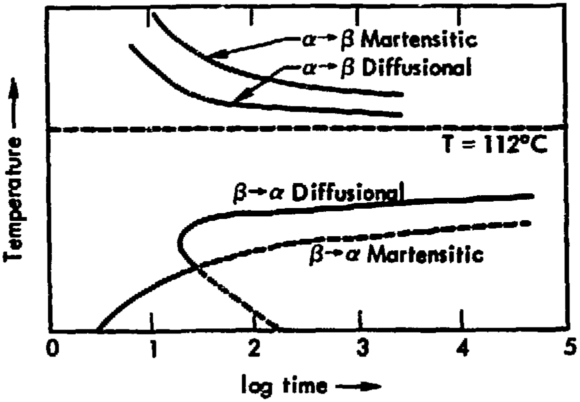

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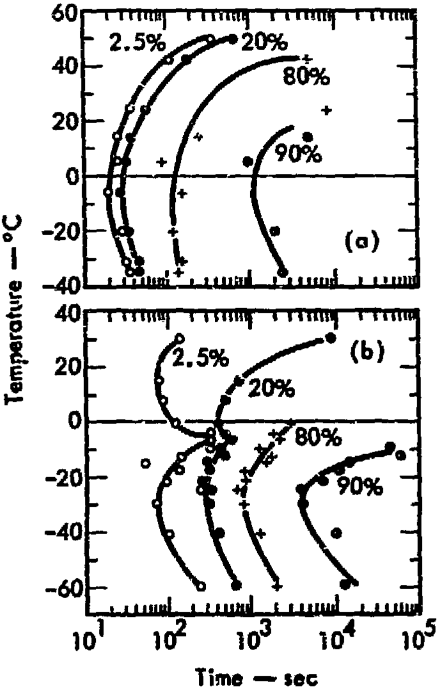
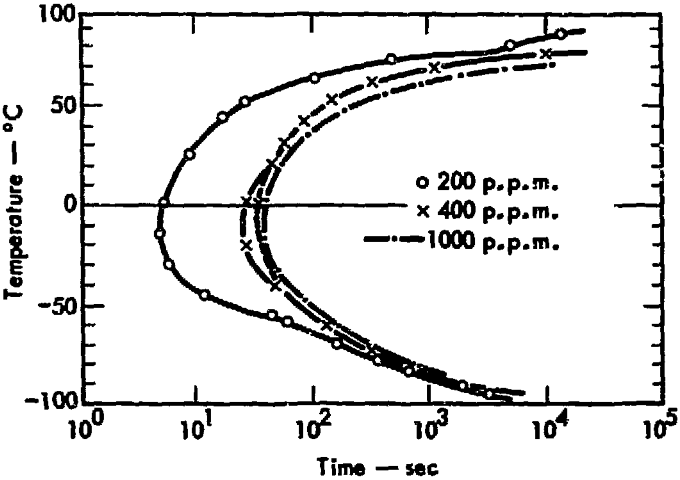


Goldberg - Fig. 6



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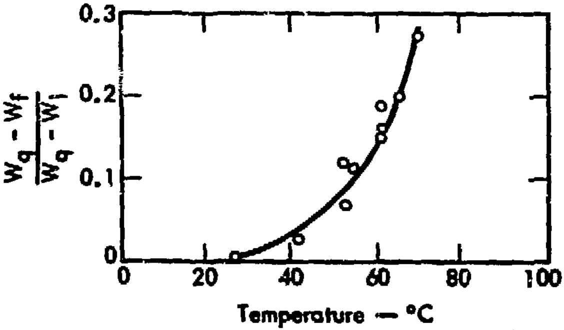

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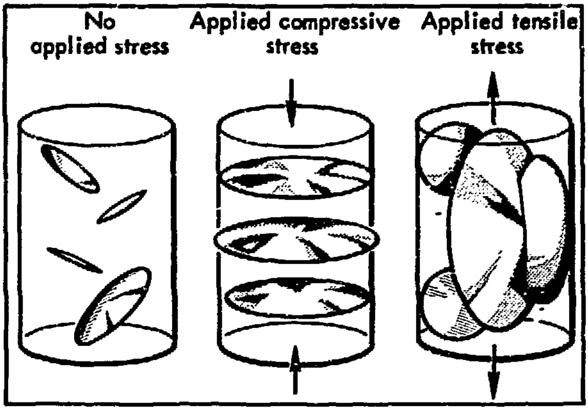

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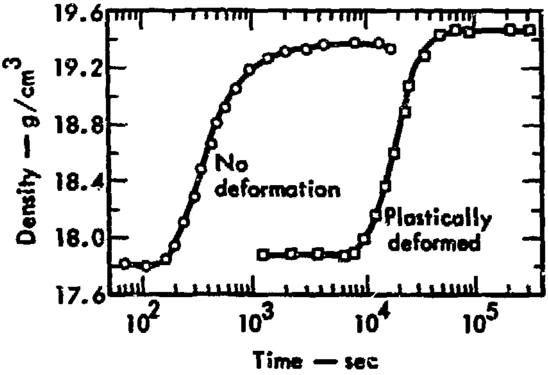

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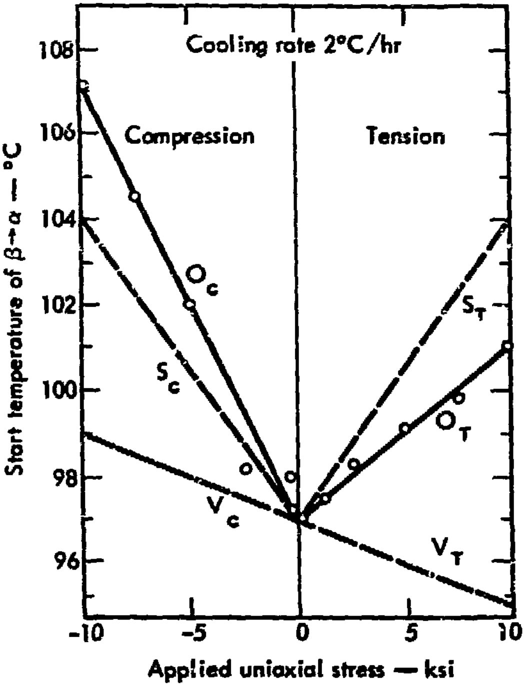

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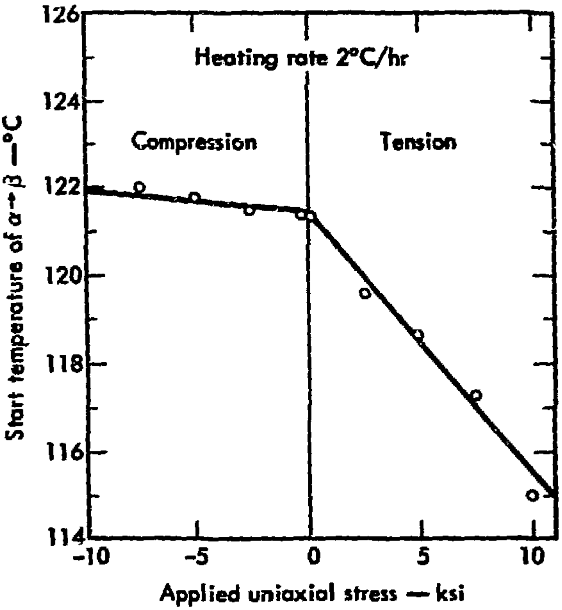

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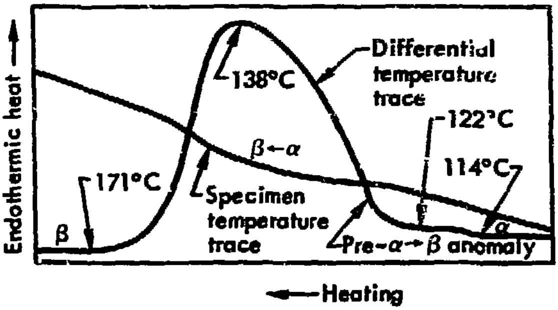

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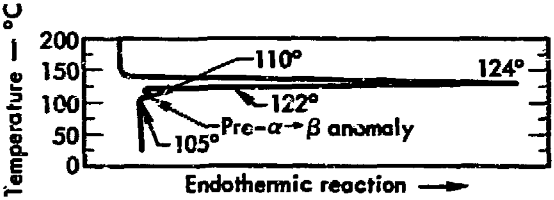

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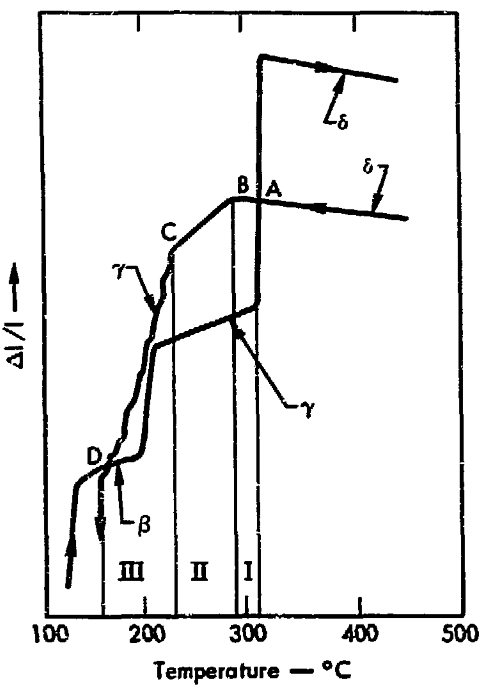

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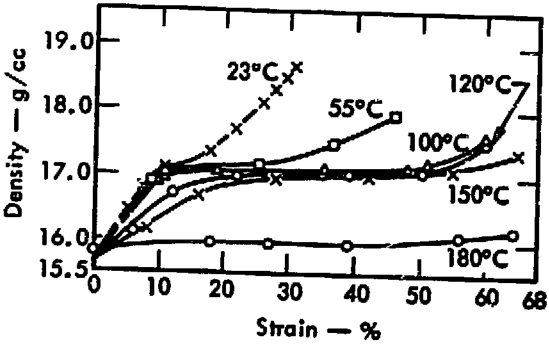

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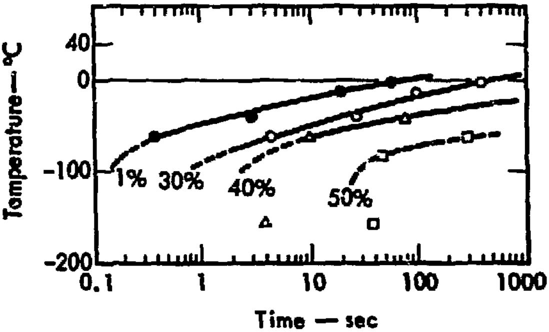

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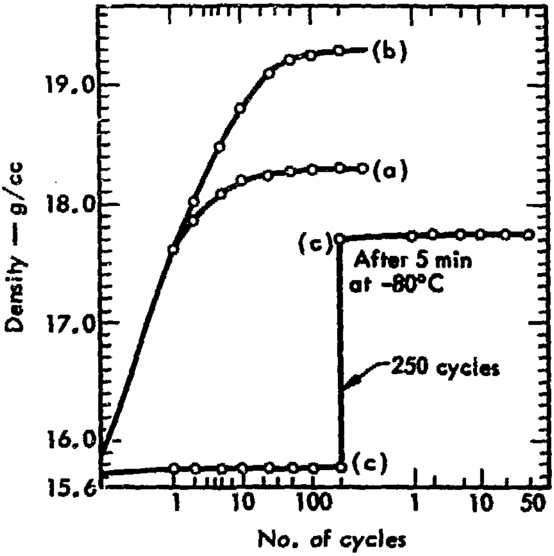

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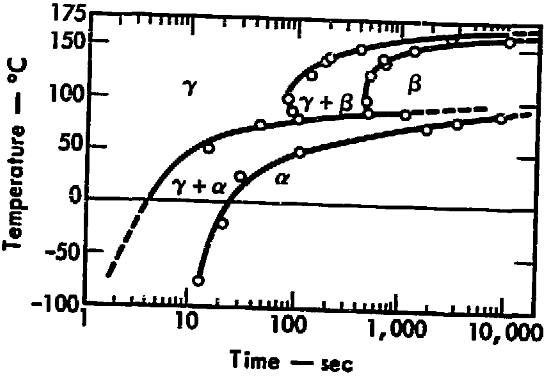

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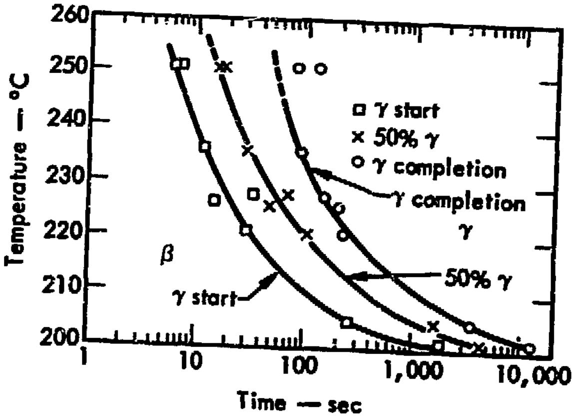

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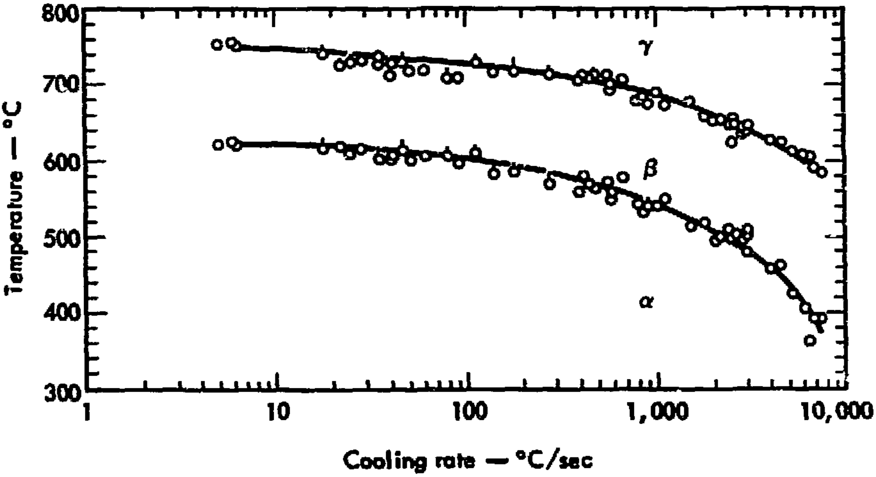

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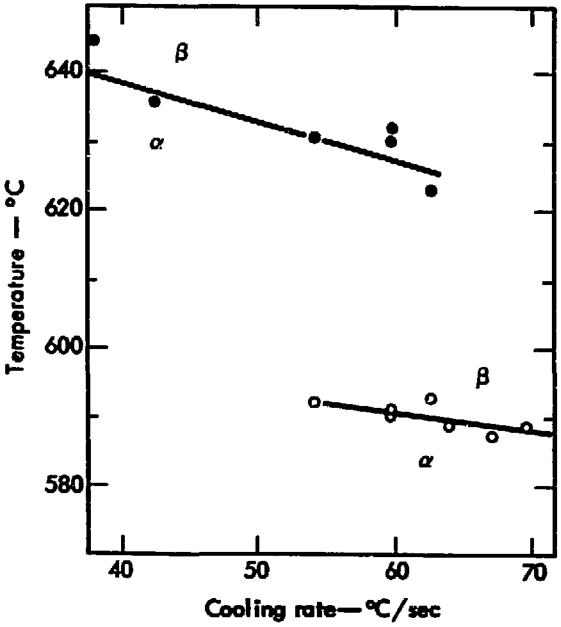

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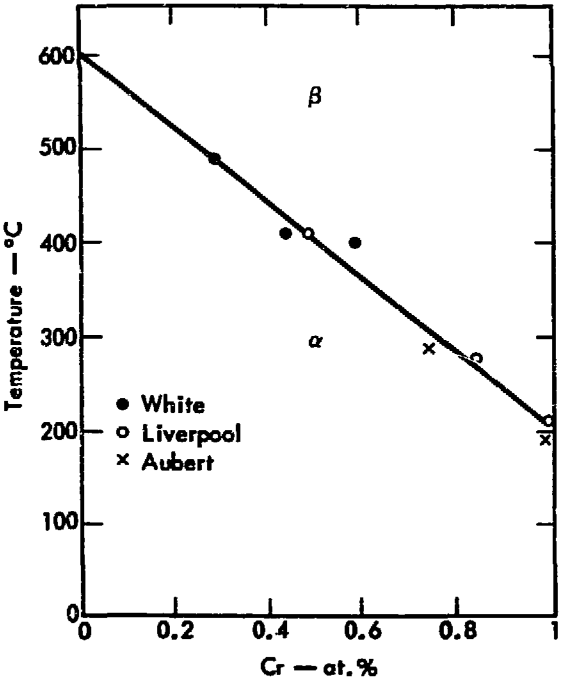

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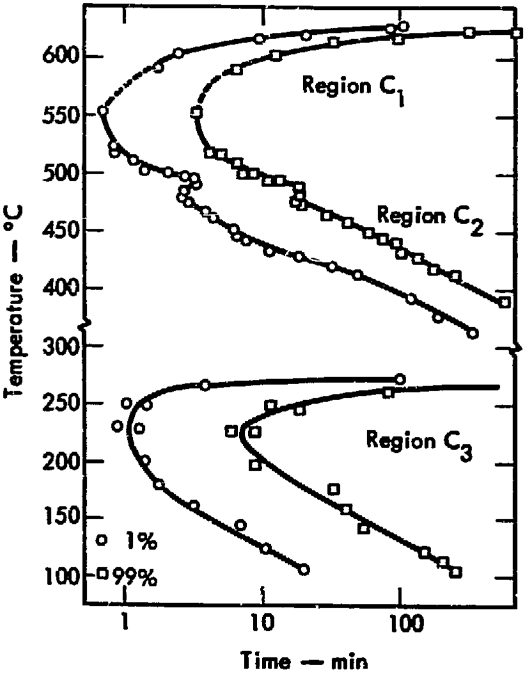

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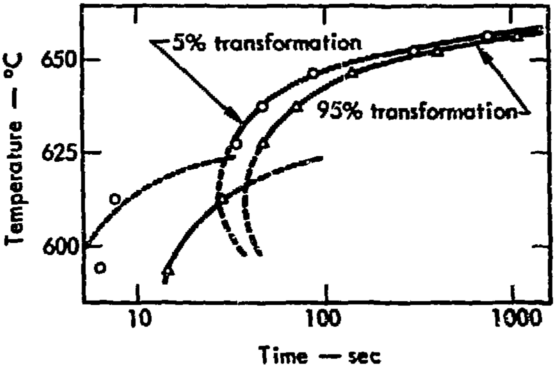

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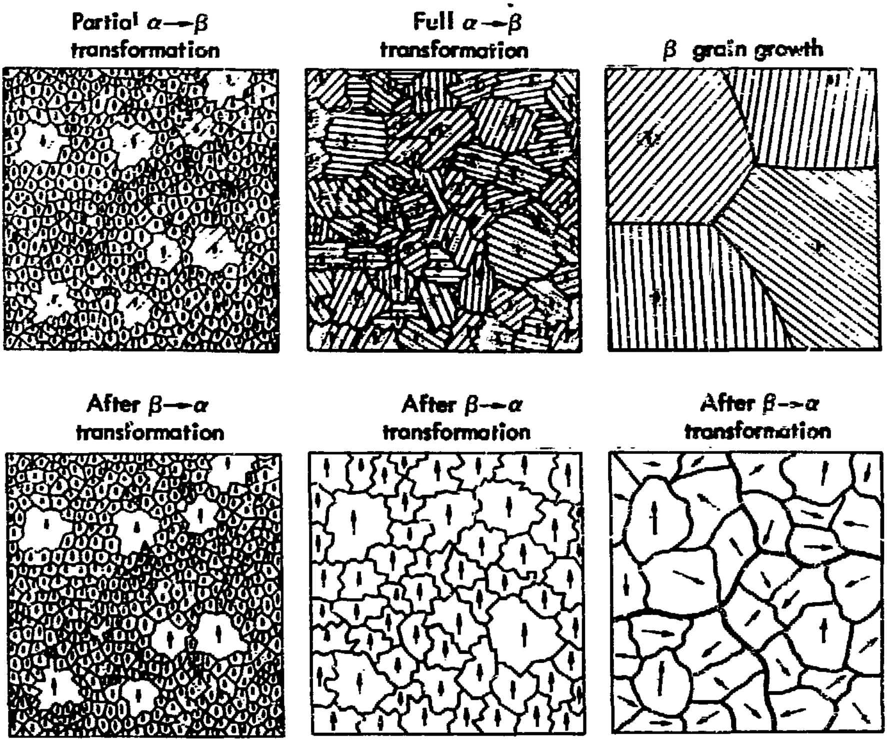
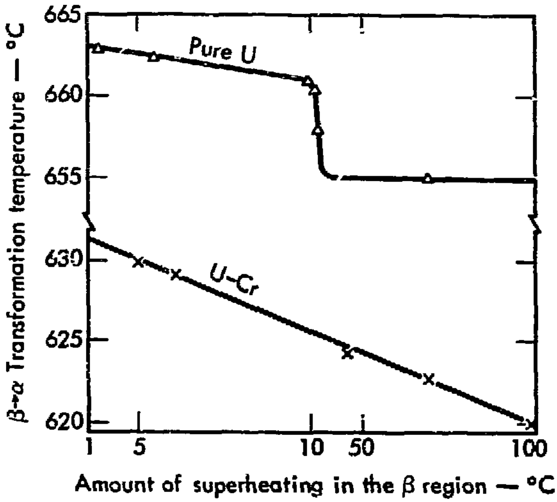


(a) (b) (c)

Goldberg - Fig. 26



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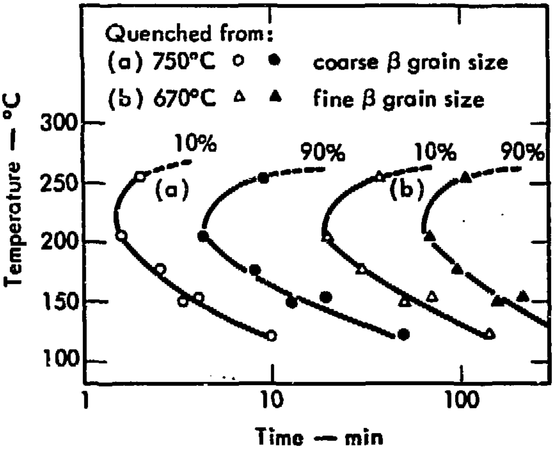
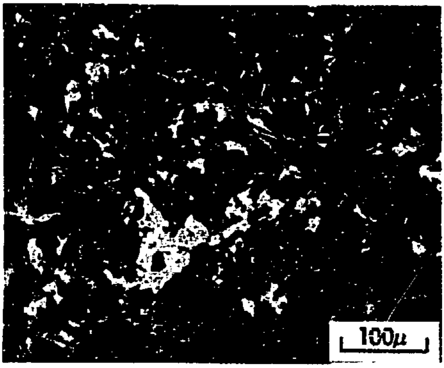


Goldherg - Fig. 28



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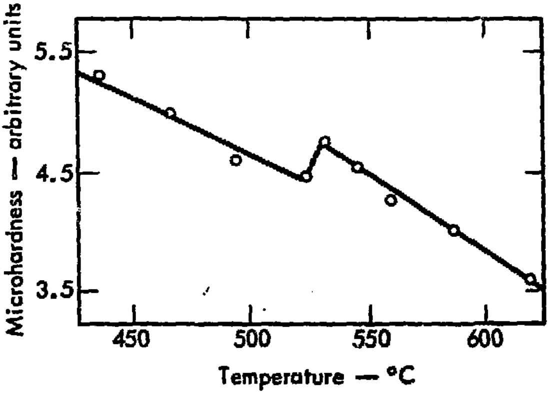

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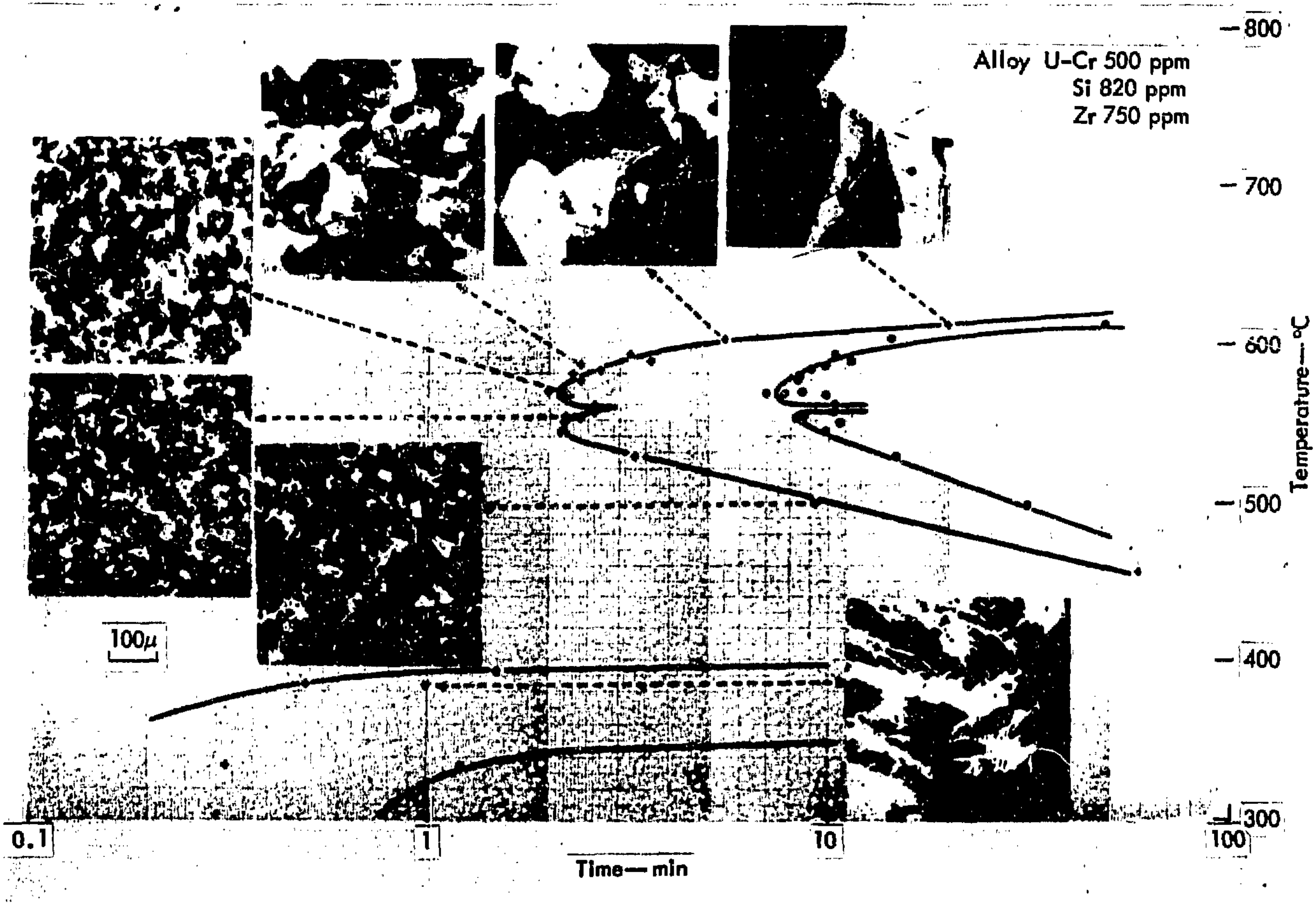

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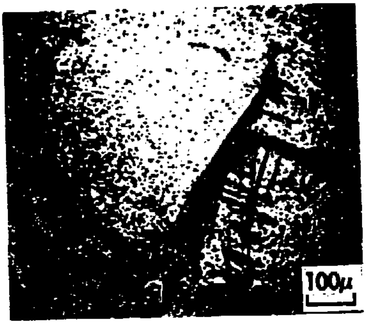

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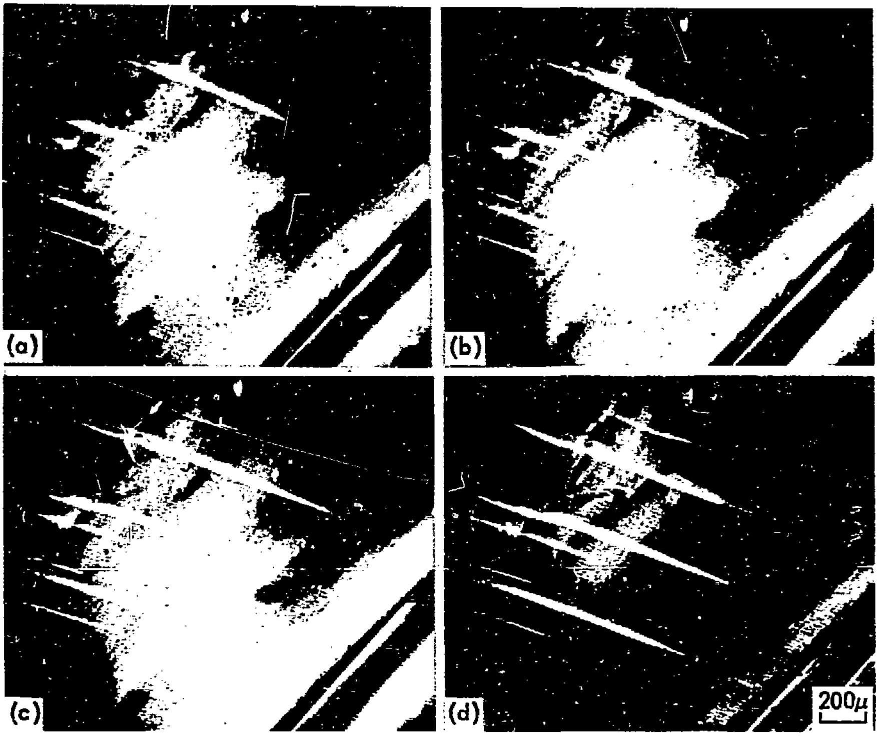

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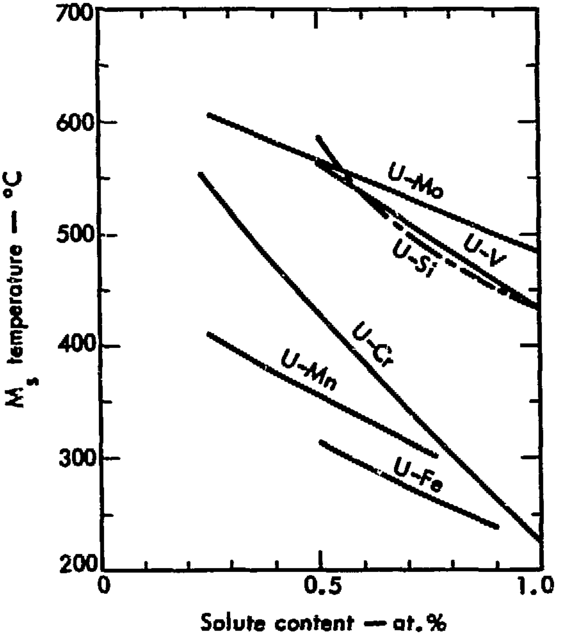

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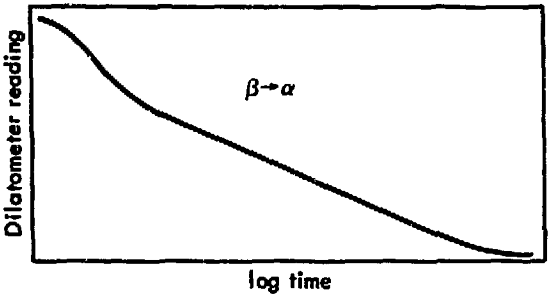

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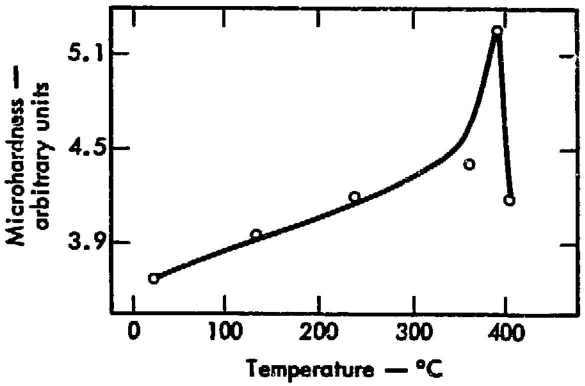

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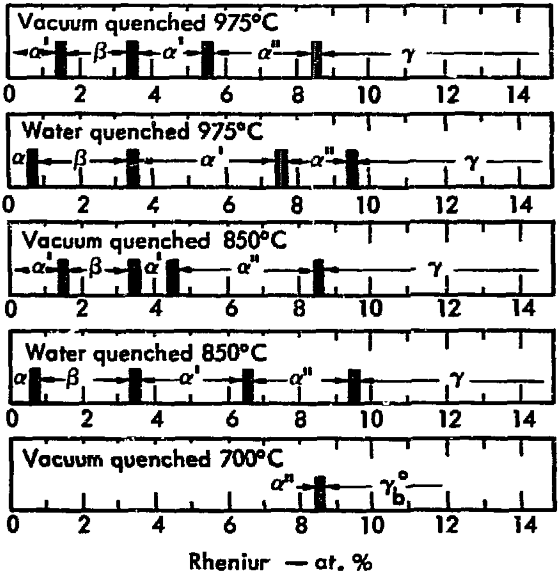

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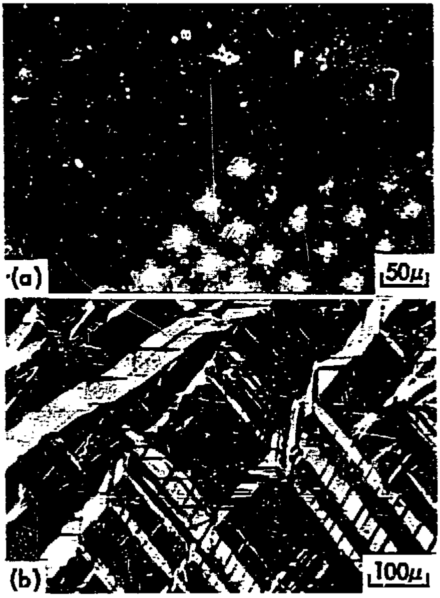
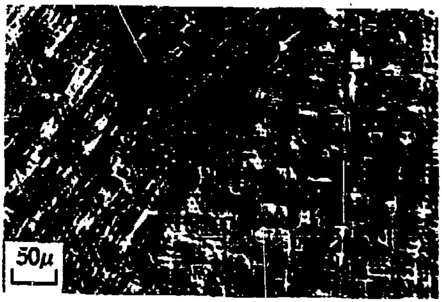


Goldberg - Fig. 38

Goldberg - Fig. 39



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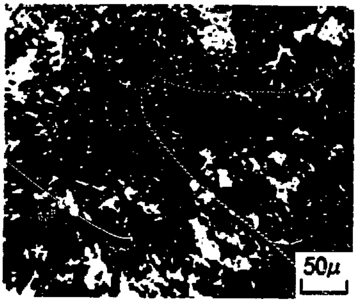

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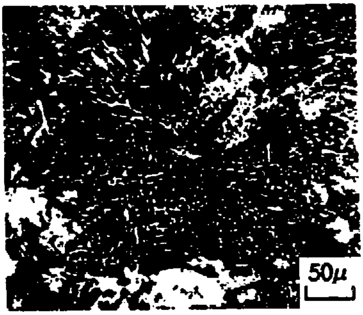
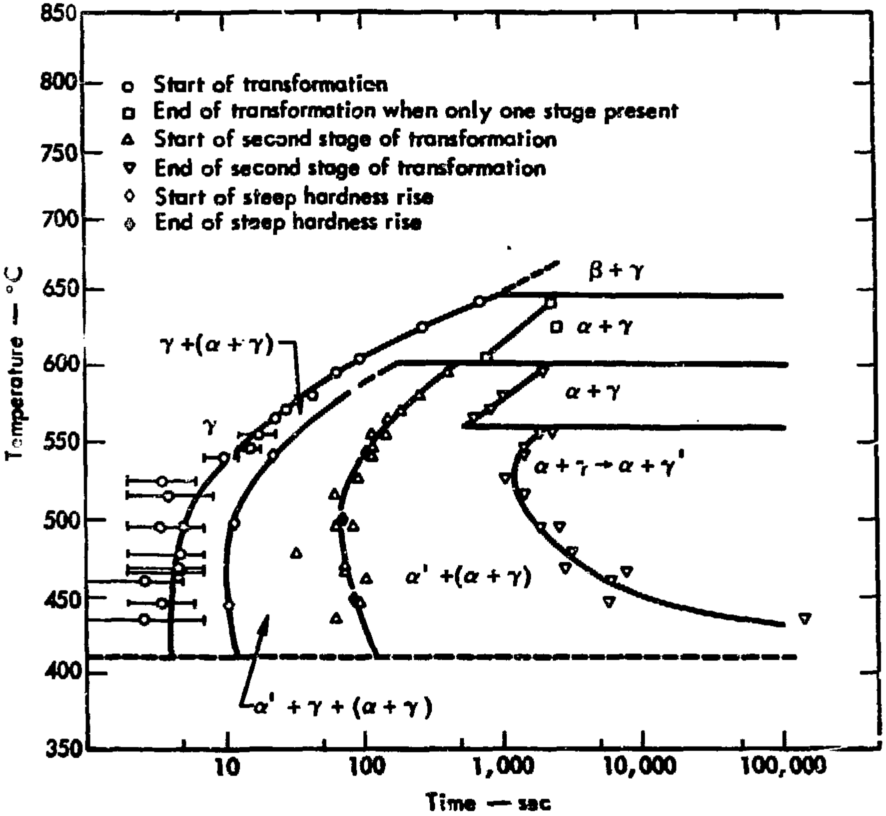


Goldberg - Fig. 42

Goldberg - Fig. 43



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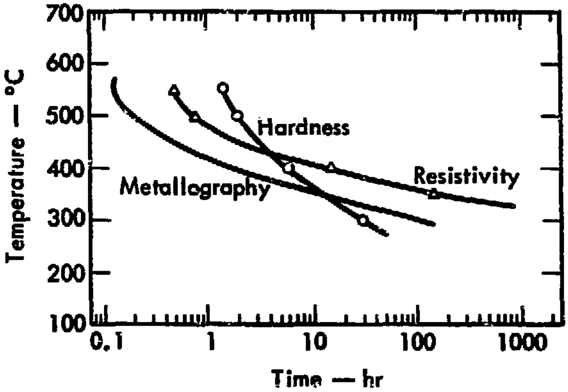

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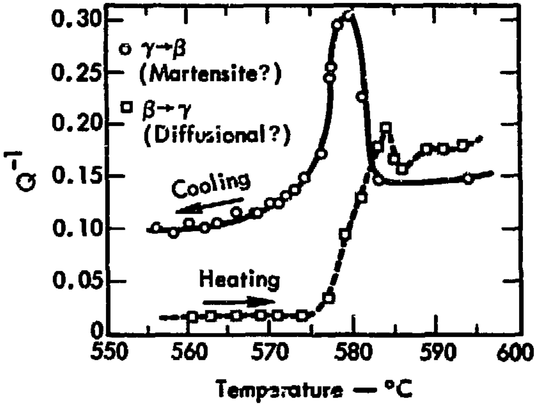

Goldberg - Fig. 46