The Effect of the Rate of Cooling on the Allotropic Transformation Temperatures of Uranium*

POL DUWEZ
California Institute of Technology, Pasadena, California, and Atomic Energy Research Department, North American Aviation, Inc., Downey, California

(Received August 11, 1952)

Allotropic transformation in uranium has been studied over a range of cooling rates from 5 to about 8000°C/sec. The transformation temperatures of both gamma-to-beta and beta-to-alpha were found to decrease continuously with increasing rates of cooling. The extent of the beta-range increased with increasing cooling rates. For rates of cooling up to 1000°C/sec, recalescence was observed in both transformations. For higher cooling rates, there was usually no recalescence.

In most of the recorded cooling curves, a small but definite thermal arrest was observed, between the two main arrests which correspond to the two known phase transformations. This additional thermal arrest was also present in a heating curve, where it occurred at about 740°C, compared with 666 and 771°C for the two known phase transformations. Possible explanations of the additional arrest are discussed.

INTRODUCTION

URANIUM undergoes allotropic transformations in the vicinity of 665 and 770°C. The low temperature form, alpha, has an orthorhombic symmetry[1] and the high temperature form, gamma, is body-centered cubic.[2] The crystal structure of the beta-form (stable between 665 and 770°C) has been recently found to be tetragonal, with 30 atoms per unit cell.[3] This structure is apparently isomorphous with that of the sigma-phase[4] found in several binary alloy systems involving the transition elements.[5–7]

TABLE I. Data on allotropic transformation of uranium.

Investigator	Transformation temperature (°C) gamma-to-beta	beta-to-alpha
Chipman (reference 8)	775	665
Dahl-Van Dusen (reference 9)		
cooling	764	645
heating	772	667
Moore-Kelley (reference 10)	772	662
Gordon-Kaufmann (reference 11)	765	772
Pfeil (reference 12)	772	665
Grogan (reference 13)		
cooling	770	660
heating	780	675
	Latent heat of transformation (cal/g at)	
Moore-Kelley (reference 10)	1165	680

The temperatures at which the alpha-to-beta and the beta-to-gamma transformations take place have been determined by several investigators.[8–13] Probably because of differences in the purity of the material as well as in the cooling or heating rate used by the various experimenters, the measured temperatures agree within only about ±10°C (see Table I). From the results published so far, however, it is not possible to ascertain whether or not the transition temperatures can be substantially depressed by increasing the rate of cooling, although it is well known that neither of the high temperature phases can be retained by quenching the pure metal to room temperature. The present investigation deals with the measurement of the allotropic transformation temperatures with rates of cooling varying from 5 to about 8000°C/sec.

EXPERIMENTAL PROCEDURE

The method for measuring transformation temperature at very fast rates of cooling consists essentially of heating a small sample of metal to which thermocouple wires are spot welded, cooling the sample by means of a jet of helium and recording the temperature *vs* time curve on an oscillograph. The apparatus used for the present experiments was similar to that described by Greninger in his study of the martensite arrest in carbon steels.[14] The retractable heating coil was made of molybdenum wire (0.04 inch in diameter) and the assembly was placed in a bell jar with a vacuum of 10^{-5} mm Hg or better.

* This paper is based on studies conducted for the U. S. Atomic Energy Commission on Contract No. AT-11-1-GEN-8. The experiments were performed with equipment constructed at California Institute of Technology under Contract No. N6onr-24430 with the Office of Naval Research, U. S. Navy.

[1] C. W. Jacob and B. E. Warren, J. Am. Chem. Soc. **59**, 2588–2591 (1937).
[2] A. S. Wilson and R. E. Rundle, Acta Cryst. **2**, 148–150 (1949).
[3] C. W. Tucker, Jr., Science **112**, 448 (1950).
[4] Dickins, Douglas, and Taylor, J. Iron and Steel Inst. **167**, 27 (1951).
[5] D. P. Shoemaker and B. G. Bergman, J. Am. Chem. Soc. **72**, 5793 (1950).
[6] P. Duwez and S. R. Baen, "X-Ray Study of the Sigma Phase in Various Alloy Systems," *Symposium on the Nature, Occurrence, and Effects of the Sigma Phase*, Spec. Tech. Pub. No. 110, Am. Soc. Testing Materials, Philadelphia, pp. 48–60, 1951.
[7] Pearson, Christian, and Hume-Rothery, Nature **167**, 110 (1951).
[8] J. Chipman, "Metallurgy in the Development of Atomic Power," U. S. Atomic Energy Commission Pub. MDDC, (1946).
[9] A. I. Dahl and M. S. Van Dusen, J. Research, Natl. Bur. Standards **39**, 53–58 (1947).
[10] G. E. Moore and K. K. Kelley, J. Am. Chem. Soc. **69**, 2105–2107 (1947).
[11] P. Gordon and A. R. Kaufmann, Trans. Am. Inst. Mining Met. Engrs. **188**, 182–194 (1950).
[12] P. C. L. Pfeil, J. Inst. of Metals **77**, 553–570 (1950).
[13] J. D. Grogan, J. Inst. of Metals **77**, 571–580 (1950).
[14] A. B. Greninger, Trans. Am. Soc. Metals, **30**, 1, 1942.

The specimens were originally made of two pieces of uranium about 0.030 inch thick and less than $\frac{1}{16}$ inch square. The 0.005-inch platinum-platinum rhodium or chromel-alumel thermocouple wires were placed between the two pieces of metal and the assembly spot welded. It was later found that when a high speed helium blast was used the two pieces were not always cooled at the same rate (probably because of the lack of symmetry in gas flow) and extraneous effects were observed. Specimens were then prepared by spot welding one small piece of uranium between two very thin platinum sheets of the same size (about $\frac{1}{16}$ inch square). In this technique, the thermocouple wires were inserted, before spot welding, between the uranium sample and the platinum covers.

The temperature was recorded on a rotating drum oscillograph.† The galvanometer was a 65-cycle-per-second element, having a resistance of 45 ohms and a sensitivity of 1-inch deflection per 25 microamperes. The instrument was calibrated by means of a Leeds and Northrup portable precision potentiometer. Records were obtained with paper speed of about $4\frac{1}{2}$ inches per second. With the exception of a few tests, a thermal arrest in the cooling curve at the transformation temperature was quite easy to locate, and the precision of measurement of the transformation temperature was approximately ± 4°C.

The quality of uranium metal used in this investigation was equivalent to that of "high purity" uranium metal, such as is available, for example, from Mallinckrodt. After most of the experiments were performed, a sample of metal was obtained which was stated to be at least as pure as the previous lot and probably of higher purity. A few additional measurements were then performed on this material, which is designated as "higher purity" metal.

RESULTS OF MEASUREMENTS ON HIGH PURITY URANIUM

About 50 cooling curves were obtained with rates of cooling ranging from 10 to 8000°C/sec. Typical curves

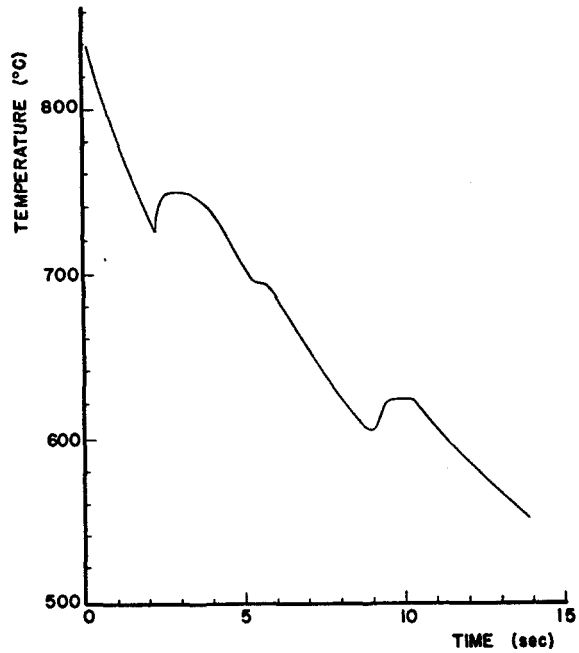

FIG. 1. Cooling curve obtained at a rate of 120°C/sec.

are shown in Figs. 1, 2, and 3. For rates of cooling up to about 1000°C/sec, a very definite recalescence was observed in many experiments, both in gamma-to-beta and in beta-to-alpha transformations (see Figs. 1 and 2). For higher rates of cooling, there was usually no recalescence, but the thermal arrests were clearly defined, as shown in Fig. 3. In the graph of Fig. 4, showing the effect of rate of cooling in the transformation temperature, recalescence is shown by a vertical line connecting the minimum temperatures corresponding to the beginning of transformation to the maximum temperature reached after recalescence. The presence of recalescence is obviously one of the reasons why the measured transformation temperatures, shown on the graph of Fig. 4, exhibit quite a large scatter. However, even at high rates of cooling, for which recalescence was not ob-

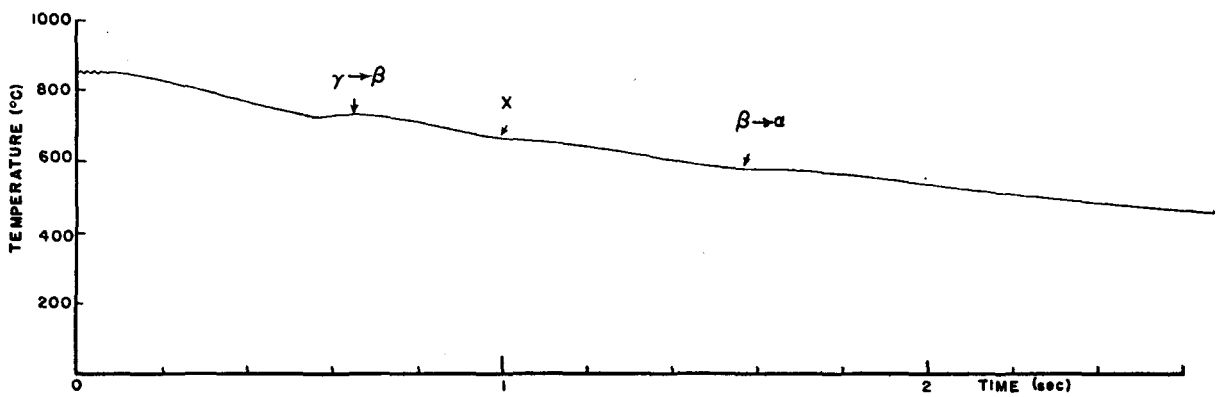

FIG. 2. Cooling curve obtained at a rate of 280°C/sec.

† Made by the William Miller Corporation, Pasadena, California.

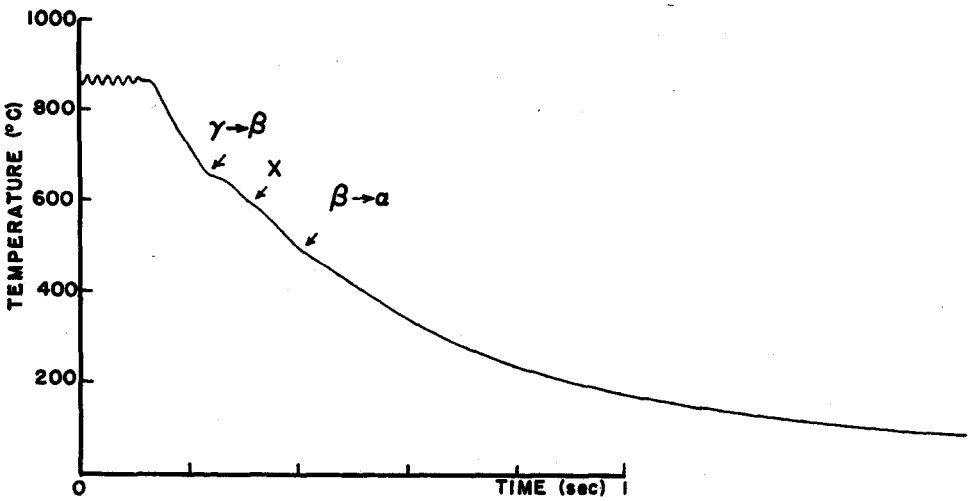

FIG. 3. Cooling curve obtained at a rate of 1800°C/sec.

served, the scatter is still greater than ±4°C, which is the estimated precision of measurement. It is probable that part of the variation in transformation temperature from specimen to specimen is due to the statistical nature of the nucleation process. In any case, all the measurements seem to be included in a band which has a width of about 30°C. By considering the center line of such a band as an average curve, it may be concluded that the gamma-to-beta transformation and the beta-to-alpha transformation temperatures of uranium decrease with increasing rates of cooling, and that the decrease is about 150°C for the gamma-to-beta transformation and about 250°C for the beta-to-alpha transformation, at cooling rates of the order of 8000°C./sec

As indicated on the graph of Fig. 4, the lowest rate of cooling used in the present study was about 5°C/sec. This rate is still much higher than that used in previous studies, from which the data presented in Table I were collected. In reference 11, for example, the rate of cooling is stated to be 1°C/min, or 0.0167°C/sec. The transformation temperature reported in reference 11 (765°C for gamma-to-beta and 655°C for beta-to-alpha), if plotted on the diagram of Fig. 4, would be two log cycles to the left of the vertical line $dT/dt=1$°C/sec. It is probable that between the rate of 0.0167°C/sec and the first point on the diagram of Fig. 4, obtained at a rate of 5°C/sec, the transformation temperature of both gamma-to-beta and beta-to-alpha decrease continuously with increasing rates of cooling.

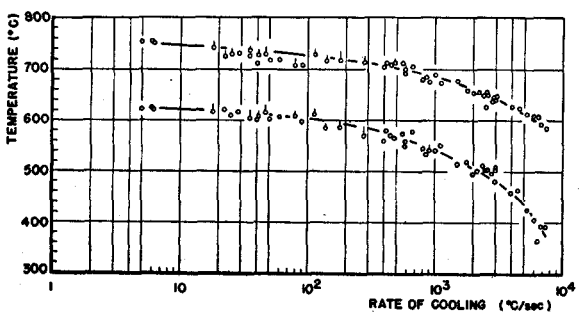

FIG. 4. Effect of rate of cooling on the allotropic transformation temperatures of uranium.

ANOMALOUS THERMAL ARREST WITHIN THE BETA-RANGE

In most of the recorded cooling curves (41 of 52 curves), a small but quite definite thermal arrest was noticed in the range of temperature between the two main arrests corresponding to the gamma-to-beta and the beta-to-alpha transformations (see point marked X in Figs. 1, 2, and 3). This extra thermal arrest was observed both in tests in which chromel-alumel thermocouples were used, as well as those in which platinum-platinum rhodium thermocouples were used. It was also present in experiments made by heating a specimen for the first time from room temperature into the gamma-field. A typical temperature-time curve obtained in these tests is presented in Fig. 5.‡

The extra thermal arrest was detected in cooling curves recorded at cooling velocities covering the entire range investigated. Within a certain scatter, which is not greater than that obtained for the two main transformation temperatures, it is apparent from the graph of Fig. 6 that the decrease in temperature of the extra thermal arrest with increasing velocity is very similar to that observed for the gamma-to-beta and the beta-to-alpha transformation temperatures (see Fig. 4).

RESULTS OF MEASUREMENTS ON HIGHER PURITY URANIUM

The results of measurements made with the higher purity uranium are summarized in Table II. For these tests, the rates of cooling were chosen so as to cover the range from 10 to 6500°C/sec. In all the cooling curves, the small thermal arrest within the beta-field was as

‡ It is interesting to note that upon heating at a rate of approximately 75°C/sec (see Fig. 5), a marked superheating effect occurs at the alpha-to-beta transformation temperature. The transformation temperatures are about 666 and 771°C, respectively. The agreement with the results obtained at a rate of 1°C/min is satisfactory (see Table I, reference 11).

clearly defined as on the curves obtained with the less pure metal. Furthermore, no significant differences were found between the transformation temperatures of the two kinds of uranium. It can be shown, indeed, that if the data given in Table II were plotted on the graphs of Figs. 4 and 6, the measured transformation temperatures of the higher purity uranium would not deviate from the previous data by more than about ±15°C. From the large number of results shown in Figs. 4 and 6, it seems that the scatter between individual measurements on the same material is also approximately ±15°C.

DISCUSSION

The results of the present investigation show that both the gamma-to-beta and the beta-to-alpha transformation temperatures are lowered when the cooling rate is increased. This result answers a question recently raised by Pfeil[12] concerning the possibility of a direct gamma-to-alpha transformation under conditions of very fast cooling. The present findings indicate that such a direct transformation is very improbable, since (at least for rates of cooling up to about 8000°C/sec) the range of temperature in which the beta-phase exists seems to increase rather than decrease with the cooling rate.

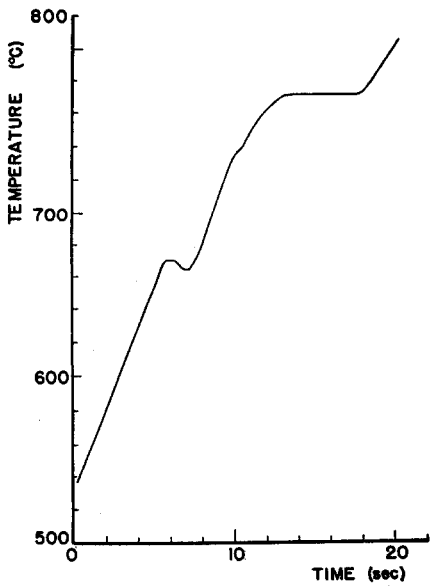

FIG. 5. Heating curve obtained at a rate of 75°C/sec.

The effect of the cooling rate on the transformation temperatures of uranium is very similar to that observed in iron, for which the gamma (face-centered cubic) to alpha (body-centered cubic) transformation temperature may be depressed by approximately 175°C when the rate of cooling is about 10 000°C/sec. In the case of iron, also, recalescence has been observed in many cooling experiments.[15] In contrast with the behavior of both uranium and iron, the allotropic transformation in the four metals having a body-centered cubic high temperature phase and a hexagonal close-packed low temperature phase (titanium, zirconium, hafnium, and thallium) has been found to be very little affected, if at all, by the rate of cooling, and no recalescence seems to take place. For titanium and zirconium,[15] a slight decrease of the order of 15 to 25°C has been observed, and for hafnium[16] and thallium[15] no measurable decrease in temperature was detected. Although all these allotropic transformations are probably diffusionless, the degree to which they are affected by the rate of cooling may indicate essential differences in the mechanism of nucleation and shear through which the transformation takes place.

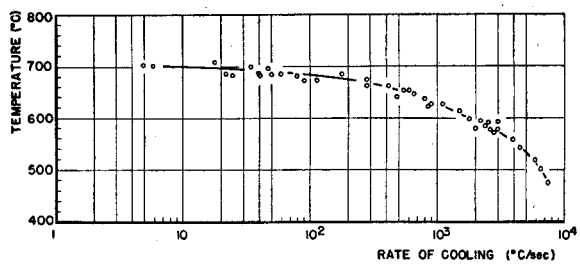

FIG. 6. Effect of rate of cooling on the temperature of thermal arrest observed within the beta-field.

The rapidity at which the high temperature gamma-phase of uranium transforms into beta and into alpha, as evidenced by the present study, suggests that the atomic displacements required for the transformation must be rather small. So far, no atomic mechanism comparable to that proposed by Burgers for the transformation in zirconium[17] has been advanced for uranium. Now that the crystal structure of beta-uranium is known, such a mechanism will probably be uncovered with the aid of a study of the crystallographic relationships among the three phases.

The existence of a thermal arrest, however small in comparison with those corresponding to the two well-established allotropic transformations in uranium, suggests at first the presence of a new allotropic transformation. A thermal arrest, however, is not enough

TABLE II. Results of measurements on high purity uranium.

Rate of cooling (°C/sec)	Transformation temperature (°C) gamma-to-beta	X	beta-to-alpha
10	735–756[a]	...	...
27	737–749	708	...
40	730–744	690	595–602
54	716–728	682	598–612
60	730–745	694	610–620
85	730–740	682	600–615
117	702–716	661	590–598
325	715–720	661	582
2500	640	586	496
6500	585	497	405

[a] Two temperatures are given when recalescence was observed.

[15] P. Duwez, Trans. Am. Inst. Mining Engrs. Met. **191**, 765–771 (1951).

[16] P. Duwez, J. Appl. Phys. **22**, 1174–1175 (1951).

[17] W. G. Burgers, Physica **1**, 561 (1934).

evidence for establishing the existence of an allotropic transformation; and, if such a transformation existed, it would be difficult to explain why previous work on uranium and uranium-base binary phase diagrams did not reveal it.[9–12] The presence of impurities in the metal is of course always a possible argument for explaining any anomalous behavior. Although two grades of uranium were used for the present experiments, it may well be that the concentration of the critical impurity in the two grades was exactly the same and consequently produced the same effect. A third possible explanation for the thermal arrest recorded in the beta-temperature range might be based on the existence of a transition similar to that recently found by Fine *et al.* in chromium.[18] Such a transition occurring at 37°C in chromium is characterized by a rather abrupt change in Young's modulus, internal friction, coefficient of espansion, electrical resistivity, and thermoelectric power, without any change in crystal structure. Further experimental work on uranium is obviously necessary before any of the preceding hypotheses may be considered as a satisfactory explanation of the observed thermal arrest.

[18] Fine, Greiner, and Ellis, Trans. Am. Inst. Mining Met. Engrs. **191**, 56–58 (1951).

CONCLUSIONS

The transformation temperatures of both gamma-to-beta and beta-to-alpha uranium decrease continuously with increasing rates of cooling, over a range from 5 to 8000°C/sec.

A small but definite thermal arrest occurs between the two main arrests, which correspond to the two known transitions. This additional arrest was observed in most of the cooling curves and also in a heating curve.

Additional experimental work is required to establish whether the observed arrest is due to the presence of a hitherto unreported allotropic transformation, to chemical impurities in the uranium, to the type of transition recently found in chromium,[18] or to some other cause.

JOURNAL OF APPLIED PHYSICS VOLUME 24, NUMBER 2 FEBRUARY, 1953

Plastic Electrets

H. H. WIEDER AND SOL KAUFMAN
National Bureau of Standards, Washington, District of Columbia
(Received September 2, 1952)

A brief discussion of proposed explanations for the electret effect is presented. Plexiglas, Lucite, and Nylon electrets were prepared under fields ranging from 19 to 36 kv/cm and observed for as long as 2000 hours. The surface charge densities were measured by electrostatic induction using a commercial electronic electrometer and a shunt capacitance to reduce the readings to a maximum of 20 volts. The initial state was a heterocharge or a homocharge depending on the strength of the forming field. The steady state was a homocharge in every case. Charge densities as high as 5.5×10^{-9} coulomb/cm^2 (16.5 esu) were observed. A Plexiglas disk was charged at room temperature under a strong field and its subsequent decaying homocharge recorded. The experimental results support the ideas of Mikola and Gross, i.e., the existence of two decaying polarizations of opposite sense due to ionic migration, one occurring within the dielectric, the other, across the electrode-dielectric interface.

I. INTRODUCTION

THE purpose of the studies described in this paper is to examine the properties of plastic electrets in the light of published information on carnauba wax electrets[1] and to clarify the basic mechanisms involved in fabrication and subsequent behavior of electrets. Relatively few investigations have been made on plastics,[2] although it is known that some exhibit the electret effect.

An electret is a dielectric which can maintain a sensibly permanent external electric field. It is usually prepared by heating and subsequent cooling of a suitable material while subjected to a high potential. Although many substances can be electrified at room temperature by means of friction or through the application of strong electric fields, the resulting surface charges tend to decay rapidly. If these substances are immersed in water or exposed to humid or highly ionized air, their charges will be irreversibly neutralized. Electrets, on the other hand, when properly stored will not decay and if neutralized as in the above manner can recover to full strength.

Many explanations for the electret effect have been proposed. Adams[3] speaks of a pyroelectric effect with a long relaxation time. Gemant[4] attributes the external field to two opposing polarizations. One arises from real ionic charges which under the forming field have concentrated at the surfaces of the electret; these

[1] See extensive bibliography in F. Gutmann, Revs. Modern Phys. **20**, 457 (1948).
[2] F. Binder, Z. Naturforsch. **6a**, 714 (1951).
[3] E. P. Adams, J. Franklin Inst. **204**, 469 (1927).
[4] A. Gemant, Phil. Mag. **20**, 929 (1935); Elect. Eng. **68**, 644 (1949).