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ZENER DISACCOMMODATION IN DILUTE F.C.C. Co-Ti ALLOYS*

H. B. AARON†‡ M. WUTTIG,†‡§ and H. K. BIRNBAUM†

The magnetic disaccommodation, i.e., the time dependence of the low field magnetic permeability, was investigated in cobalt base alloys containing 0–5.1 at. % (0–4.2 wt. %) titanium in the temperature range 400–700°C. A strong temperature dependence of the disaccommodation observed in the range 430–530°C could be accounted for predominantly by a single first order relaxation process. Analyzing the data in terms of (a) a single exponential relaxation, (b) a lognormal distribution of relaxation times, and (c) a sum of exponential relaxations, it was shown that the relaxation strength varies as the square of the titanium concentration and that the relaxation is characterized by an activation enthalpy of 69 ± 1 kcal/mole and a τ_0 of the order of 10^{-16} sec. The disaccommodation was attributed to the reorientation of substitutional solute atom (titanium) pairs. From the temperature dependence of the relaxation strength the binding energy of Ti atom pairs was determined to be 0.17 ± 0.08 eV.

DESAJUSTEMENT ZENER DANS LES ALLIAGES DILUES Co-Ti C.F.C

On étudie le désajustement magnétique, i.e l'influence du temps sur la perméabilité magnétique à bas champ, dans des alliages à base de cobalt contenant 0–5,1 at. % (0–4,2 % en pds) de titane dans le domaine de températures 400–700°C. On observe une forte influence de la température sur le désajustement dans le domaine 430–530°C; on peut en rendre compte principalement par un processus de relaxation simple du premier ordre. En analysant les données (a) en termes d'une relaxation exponentielle simple (b) en termes d'une distribution lognormale des temps de relaxation, et (c) en termes d'une somme de relaxations exponentielles, on montre que la force de la relaxation varie comme le carré de la concentration en titane et que la relaxation est caractérisée par une enthalpie d'activation de 69 ± 1 kcal/mole et par un τ_0 de l'ordre de 10^{-16} sec. Le désajustement est attribué à la réorientation de paires d'atomes de soluté (titane) en substitution. A partir de l'influence de la température sur la force de la relaxation, on détermine l'énergie de liaison des paires d'atomes de Ti: $0,17 \pm 0,08$ eV.

ZENER DESAKKOMMODATION IN VERDÜNNTEN k.f.z. Co-Ti LEGIERUNGEN

Die magnetische Desakkommodation, d.h. die Zeitabhängigkeit der Permeabilität bei schwachem Magnetfeld, wurde in Kobaltlegierungen mit 0–5,1 At.-% (0–4,2 Gew.-%) Titan im Temperaturbereich 400–700°C untersucht. Eine starke Temperaturabhängigkeit der Desakkommodation im Bereich 430–530°C konnte als einfacher Relaxationsprozess erster Ordnung beschrieben werden. Die Ergebnisse wurden als (a) eine einfache exponentielle Relaxation, (b) eine lognormale Verteilung von Relaxationszeiten und (c) als eine Summe von exponentiellen Relaxationszeiten analysiert. Es zeigte sich, dass die Relaxationsstärke sich mit dem Quadrat der Titankonzentration ändert und dass die Relaxation durch eine Aktivierungsenthalpie von 69 ± 1 kcal/Mol und durch ein τ_0 in der Größenordnung 10^{-16} sec charakterisiert ist. Die Desakkommodation wird der Reorientierung substitutioneller Fremdatompaare (Titan) zugeschrieben. Aus der Temperaturabhängigkeit der Relaxationsstärke ergibt sich die Bindungsenergie zweier Titanatome zu $0,17 \pm 0,08$ eV.

1. INTRODUCTION

1.1 Zener relaxation

The term "Zener relaxation" has been used to denote the anelastic relaxation phenomena associated with the stress-induced changes in substitutional solute atom distributions first observed by Zener⁽¹⁾ in alpha-brass and later observed by others in a variety of substitutional solid solutions. The relaxations have been interpreted in terms of the stress-induced

reorientation of solute atom pairs^(2,3) and in more general terms as stress induced ordering.⁽⁴⁾ The interpretation of the Zener relaxations in terms of the reorientation of solute atom pairs can only be valid for small solute concentrations since the concept of individual solute pairs has meaning only at low solute concentrations. However, as a result of the small relaxation strength and the low binding energies of the solute atom pairs, relatively high concentrations (in excess of 10% solute) are usually required in order to observe the Zener relaxations in an internal friction experiment. The alternative model⁽⁴⁾ for the Zener relaxation based on the assumption that the short range order parameters in the various crystallographic directions of the crystal are dependent on the applied stress applies for all solute concentrations.

The experimentally determined concentration dependence of the Zener relaxation strength has been shown to fit both the C^2 dependence of the Zener⁽²⁾

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theory and the $C^2(1 - C)^2$ dependence of the LeClaire-Lomer⁽⁴⁾ theory. Both theories fail to explain the experimentally observed anisotropy of the Zener relaxation^(5,6) in f.c.c. and b.c.c. alloys. As discussed by Berry⁽⁵⁾ this appears to be due to the inadequacy of the assumption that it is sufficient to describe the atomic configuration in terms of the pair-wise grouping of nearest neighbors. It has been suggested by Seraphim and Nowick⁽⁶⁾ that relaxations resulting primarily from the reorientation of second-nearest-neighbor pairs appear to be capable of explaining the observed results.

The anelastic measurements of Zener relaxation have been carried out on concentrated alloys with the exception of the measurements on Al + 1.78 at. % Cu.⁽⁵⁾ In this alloy it is estimated that about 75% of the relaxation strength is attributed to isolated solute pair reorientation. It is of interest to extend the measurements to still lower solute concentrations where essentially all pairs are isolated and to repeat the above observations on another alloy system. Since the anelastic relaxation strength per atomic percent solute is generally too small to use dilute alloys, other techniques for investigating these phenomena are required. In the present investigation a magnetic technique is described and applied to cobalt-titanium alloys.

1.2 Time dependent magnetic measurements

Defects and solute atom clusters whose symmetry is lower than the point group symmetry of the lattice⁽⁷⁾ will in general interact with the spontaneous magnetization of a ferromagnetic solid causing time dependent variations in the initial magnetic permeability (disaccommodation).⁽⁸⁾ This interaction which may result from magnetocrystalline strains⁽⁹⁻¹¹⁾ and/or from an electronic interaction via the spin-orbit coupling of the $3d$ electrons,⁽¹²⁾ causes a tendency for preferential orientation of the defects or a preferential occupation of certain lattice sites relative to the magnetization direction of each domain. After a suitable demagnetization procedure which randomizes the domain boundaries or the defect (solute atom cluster) orientations or both, it is observed that the initial permeability decreases with time as the system minimizes its free energy by redistribution of the defects (solute clusters). This disaccommodation reflects the kinetics of motion of the lattice defects or solute atom clusters. The disaccommodation, while analogous to the elastic aftereffect, generally has a higher sensitivity. In f.c.c. solids it reflects the behavior of solute atom pairs or higher order clusters since the strain field of a single substitutional solute atom

has cubic symmetry. Previous disaccommodation studies have been reviewed by Adler and Radloff.⁽¹³⁾

Magnetic relaxations attributed to the reorientation of substitutional solutes (magnetic Zener effect or Zener disaccommodation) have not been well established. Some work has been done on the b.c.c. Fe-Si,^(14,15) Fe-Al,⁽¹⁶⁾ and Fe-Ni⁽¹⁷⁾ systems. The existence of an interaction between the spontaneous magnetization and the distribution of substitutional solute atoms has been shown by measurements of magnetization curves, resistivity, magnetoresistance, residual magnetization, and the initial permeability on polycrystalline Ni-21.5% Fe⁽¹⁸⁻²⁰⁾ and on Ni-Co alloys.⁽²¹⁾ Suzuki's observations⁽²²⁾ on the orientation dependence of magnetic annealing in b.c.c. Fe₃Al showed that the effects of second-nearest-neighbor interactions must be included to explain the observations.

The present work is part of a study of magnetic measurements of Zener relaxations (Zener disaccommodations) in dilute f.c.c. alloys. The Co-Ti system was chosen for the current study since Co is f.c.c. above about 420°C and has a high Curie temperature (1100°C); Ti dissolves substitutionally with a limited solid solubility range and a nearly vertical solvus line below about 700°C.⁽²³⁾

2. EXPERIMENTAL PROCEDURE

2.1 Measurement of the permeability

The initial magnetic permeability, μ_i , was determined by measuring the mutual inductance of a coil containing the specimen as a core using a self balancing a.c. bridge⁽²⁴⁾ (Fig. 1). The amplified unbalance signal from the bridge was fed into a recorder which adjusted one bridge resistor to null the unbalance signal. Using a lock-in amplifier and tuned circuitry in the control loop, the relative initial permeability of the Co-Ti alloys could be measured

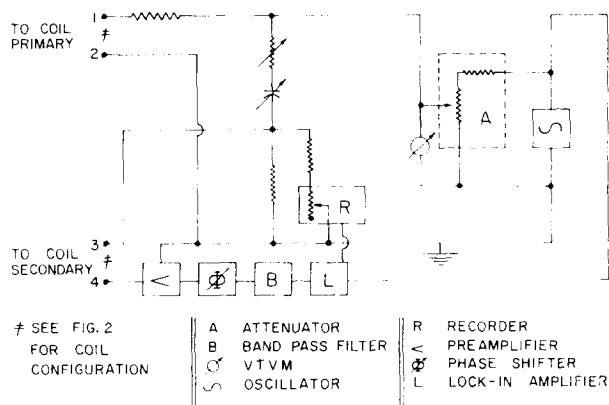


Fig. 1. Furnace and temperature control system.

with a precision of 5 parts in 10^5 at a measuring field of 7 mOe and a bridge frequency of 271 c/s. The earth's magnetic field at the specimen was cancelled by the field of a Helmholtz coil.

In order to randomize the solute atom clusters with respect to spontaneous magnetization direction, the specimens were demagnetized at the start of each relaxation by gradually decreasing a 60 cycle field from 50 Oe to below the measuring field in steps of 1/2 mOe. It was necessary to demagnetize several times before each measurement in order to completely randomize the domain walls with respect to the solute atom clusters. The demagnetization procedure caused no upset of the temperature balance and repeated relaxation measurements started in this fashion were reproducible to within the measuring accuracy. The uncertainty in the time at which the relaxation began after demagnetization was about 0.2 sec. Measuring fields between 1.5 mOe and 150 mOe gave identical disaccommodation results indicating that the effect was not dependent on the amplitude of the domain boundary displacement. The 7 mOe measuring field was well within the reversible permeability range, i.e. the domain wall oscillated about a fixed equilibrium position with an amplitude of oscillation so small that it had no measurable effect on the distribution of solute atom cluster orientations. The measuring field frequency of 271 c/s was sufficiently low to make eddy current losses negligible and gave a good signal to noise ratio.

A measuring coil⁽²⁵⁾ wound with Anaconda CS-1200 nickel clad silver wire on an Al_2O_3 tube was used. The primary-secondary insulation resistance of the coil was greater than 250 k Ω at 700°C. The contribution to the permeability measurement due to this leakage resistance was negligible (less than 1 part in 250,000).

The measurements which required good temperature control were performed in a vacuum furnace which was noninductively wound and heated by a low current (less than 2 A) high voltage (up to 500 V) d.c. supply with an a.c. ripple of less than 2 mV. The a.c. magnetic field caused by this ripple was negligible compared to the 7 mOe measuring field. This arrangement allowed temperature control of $\pm 0.1^\circ C$ at 700°C with a temperature gradient along the 2 inch specimen length of less than $0.01^\circ C$. Temperature was measured using a Pt-Pt + 10% Rh thermocouple in contact with the specimen.

2.2 Specimen preparation

The specimens were prepared by inductively melting 99.998% pure Johnson Matthey cobalt doped

with varying amounts of 99.99% pure United Mineral titanium in 99.98% pure recrystallized alumina crucibles under a vacuum of better than 2×10^{-6} torr. Wet chemical and spectroscopic analyses showed less than 0.01 wt.% variation in titanium concentration along the specimen length, aluminum pickup of about 0.1 wt.%, and oxygen pickup of less than 100 ppm in all cases. The grain size was kept large and constant at about 10 grains per specimen to eliminate problems due to grain boundary relaxations. The pure cobalt specimens were prepared by annealing the Johnson Matthey rods under a static vacuum of better than 10^{-6} torr for 3 days at 1000°C.

3. DATA ANALYSIS AND RESULTS

3.1 Permeability and disaccommodation results

Measurements of the initial permeability, μ_i , of the Co-Ti alloys in the temperature range 400–700°C showed strong history, concentration, and temperature dependences. The history dependence of the initial permeability determined at a given time after demagnetization (Figs. 2 and 3) was characterized by an irreversible decrease in the magnitude of the permeability during the heating and cooling cycles. This decrease in μ_i occurred isothermally as well as during the heating and cooling cycles (Fig. 4). The maximum in μ_i at about 470°C for the alloy specimens

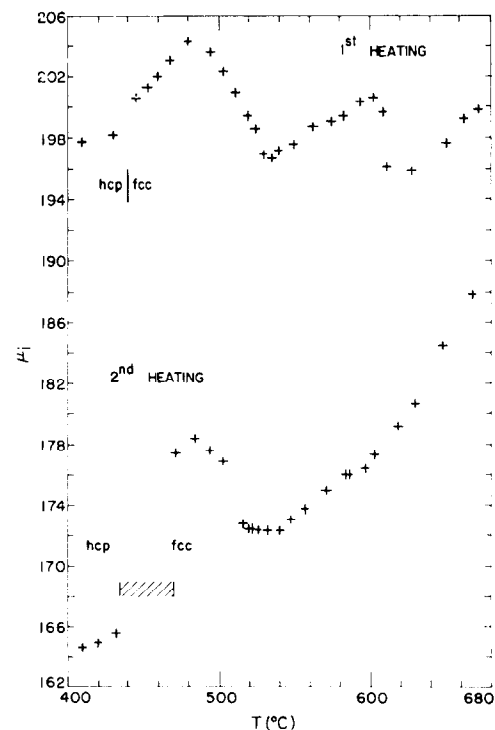


Fig. 2. Initial permeability at 1 min after demagnetization as a function of temperature for the 2.5 wt.% Ti alloy during the 1st and 2nd heating through the transformation.

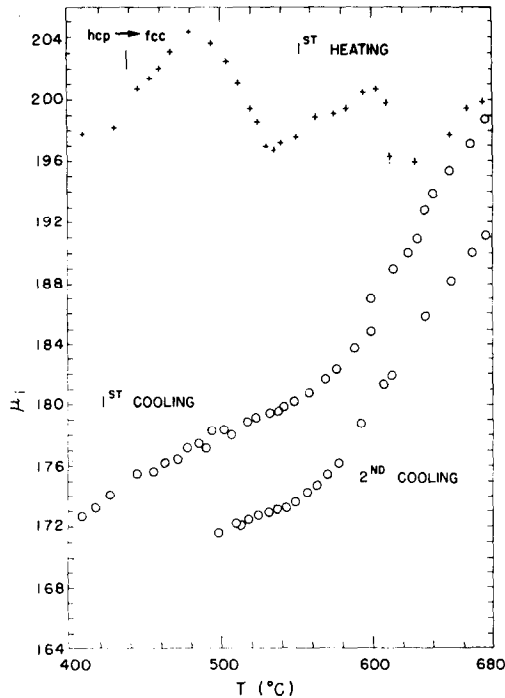


FIG. 3. Initial permeability at 1 min after demagnetization as a function of temperature for the 2.5 wt. % Ti alloy during the 1st (O) and 2nd (O) cooling cycle and the 1st heating (+) through the transformation.

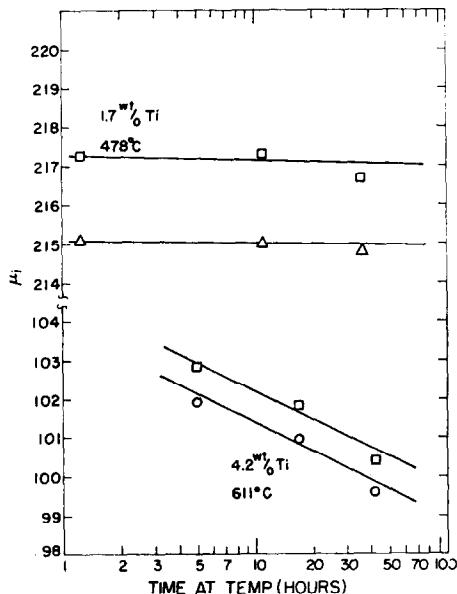


FIG. 4. Initial permeability vs. time at temperature at zero (□), 15 (Δ), and 60 (○) minutes after demagnetization for the 1.7 wt. % Ti alloy at 478°C and the 4.2 wt. % Ti alloy at 611°C.

(Fig. 2) was associated with the h.c.p. \rightarrow f.c.c. transformation as shown by the observation that it was not present in the cooling curves (Fig. 3) or on heating from 440°C without going through the transformation. Similar results are found in pure Co (see Appendix). The f.c.c. \rightarrow h.c.p. transformation was

not observed in the alloys on decreasing the temperature to 400°C indicating that the transformation occurred below 400°C on cooling. In addition to this hysteresis in transformation temperature the h.c.p. \rightarrow f.c.c. transformation became progressively more sluggish each succeeding time through the transformation (Fig. 2). For the 2.5 wt. % Ti alloy shown, which is typical of all alloys studied, the transformation occurred over the range 435–470°C during the second heating cycle. Data were not taken during the transformation due to complications arising from the presence of varying amounts of the two phases.

The initial permeability was found to decrease with time at temperature (Fig. 4); the rate of decrease being greater at higher temperatures and/or higher solute concentrations. As will be discussed in more detail later, this variation in the absolute magnitude of μ_i was found to have no effect on the observed disaccommodations, i.e., $1/\mu_i(t_2) - 1/\mu_i(t_1)$ was found to be independent of time at temperature in the range 400°C to 625°C (Fig. 4). The magnitude of the initial permeability of specimens having equivalent previous histories decreased with increasing Ti concentration (Fig. 5). The variation of μ_i with the Ti concentration was much greater than the changes observed on successive heating and cooling cycles (Fig. 5). Furthermore, as shown in Fig. 5, the temperature dependence

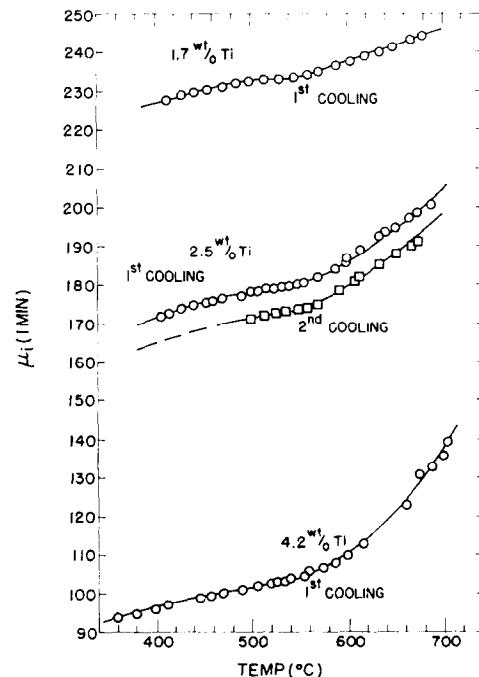


FIG. 5. Initial permeability 1 min after demagnetization as a function of temperature for Co-1.7 wt. % Ti, Co-2.5 wt. % Ti, and Co-4.2 wt. % Ti during the 1st cooling cycle after heating through the transformation and annealing at 700°C *in situ*, and for Co-2.5 wt. % Ti during the 2nd cooling cycle after the 2nd transformation and anneal.

of μ_i was more pronounced the higher the titanium concentration.

Strongly temperature dependent disaccommodations were observed to be superimposed on the above variations of μ_i for the Co-Ti alloys in the range 400–700°C (but not for the pure cobalt specimens as shown in the Appendix). Typical data are summarized in Fig. 6 for several temperatures and compositions. The characteristics of this disaccommodation were

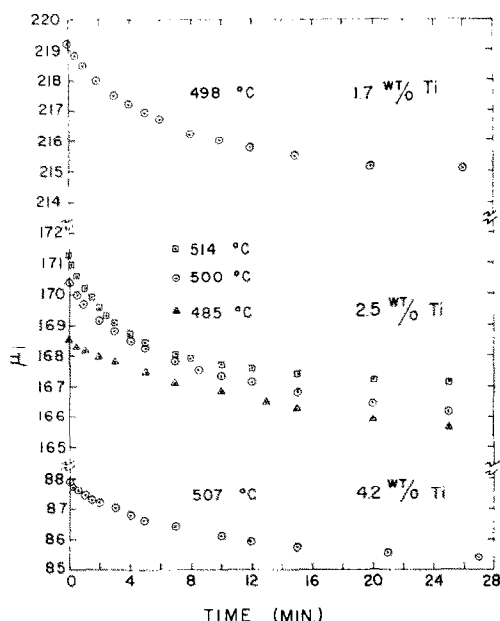


Fig. 6. Disaccommodation of the initial permeability for various temperatures and Ti compositions.

determined by measuring the initial permeability at two times after demagnetization. With the zero of time taken when the demagnetizing field became smaller than the measuring field, μ_i at 1 and 5 min was measured as a function of temperature and composition. The magnitude of the disaccommodation is characterized by the reluctivity difference $1/\mu_i(5) - 1/\mu_i(1)$. For thermally activated processes the temperature dependence of the reluctivity difference resulted from the fact that at low temperatures the relaxation occurred slowly and $1/\mu_i(5) - 1/\mu_i(1)$ approached zero. At higher temperatures an appreciable portion of the disaccommodation occurred in the time interval 1–5 min resulting in a large difference in reluctivities. At still higher temperatures the relaxation proceeded at such a rapid rate that it was essentially completed before 1 min again resulting in a small value for the reluctivity difference.

After annealing at 700°C for 1/2 hr a pronounced disaccommodation peak at about 520°C was observed on heating and on cooling (Fig. 7). The magnitude of this peak was increased by about a factor of 2 after

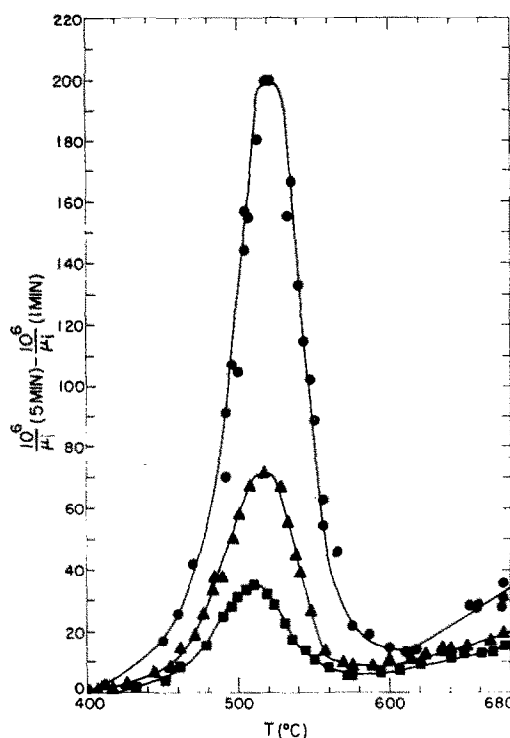


Fig. 7. Variation of reluctivity difference with temperature on the 1st cooling after an anneal for 1/2 hr at 700°C *in situ* for the 4.2 (●), 2.5 (▲), and 1.7% (■) Ti alloys.

the 1/2 hr anneal at 700°C as compared to the peak magnitude observed on first heating after a phase transformation. Its magnitude was decreased slightly during successive cooling cycles each of which was preceded by a phase transformation and annealing at 700°C *in situ* (Fig. 8). This slight decrease in peak height was accompanied by an attendant increase in the high temperature background. These disaccommodation peaks were not observed in pure cobalt (see Appendix).

Metallography and microprobe analyses were carried out to help explain these phenomena and will be reported later. For the present, attention will be focussed on the peak observed at about 520°C on cooling after an anneal at 700°C. This peak was investigated by taking $1/\mu_i(5) - 1/\mu_i(1)$ vs. temperature spectra over the range 700–400°C and by obtaining isothermal relaxation curves, μ_i vs. time, at various temperatures in the range 530–430°C: the upper limit being imposed by the need to have the relaxation proceed slowly enough to obtain $\mu_i(t=0)$ and the lower limit by the prohibitively long relaxation times at lower temperatures. The temperature spectra and isothermal relaxation data were analyzed in three different ways:

- (a) as a single exponential relaxation having an activation enthalpy, Q , and relaxation time, τ ,

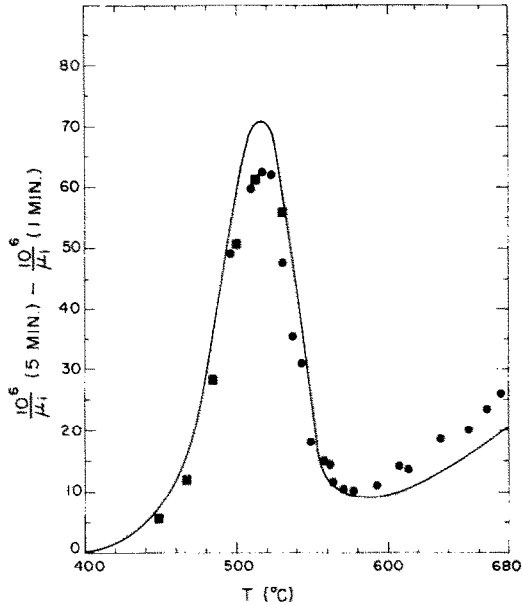


Fig. 8. Variation of relativity difference with temperature for the 2.5 wt.% Ti alloy. Points are $1/\mu_i$ (5) — $1/\mu_i$ (1) data (●) and isothermal runs (■) on the 2nd cooling after the 2nd cycle through the h.c.p. → f.c.c. transformation and the second 1/2 hr anneal at 700°C *in situ*. The solid curve shows the same type of data taken during the 1st cooling after a 1/2 hr anneal at 700°C.

- (b) as a single relaxation with a lognormal distribution of relaxation times, and
 (c) as a sum of exponential relaxations.

3.2 Single exponential relaxation analysis

If the disaccommodation results from a sum of several first order relaxation processes one can write

$$\frac{1}{\mu_i(\infty)} - \frac{1}{\mu_i(t)} = \sum_j a_j \exp\left(-\frac{t}{\tau_j}\right) \quad (1)$$

where a_j and τ_j are respectively the relaxation strength and relaxation time of the j -th relaxation. Generally a_j is a function of temperature and

$$\tau_j = \tau_{0j} \exp\left(\frac{Q_j}{RT}\right). \quad (2)$$

The activation enthalpy for the j -th relaxation process is Q_j and the preexponential is

$$\tau_{0j} = Z\nu^{-1} \exp\left(-\frac{\Delta S_j}{R}\right) \quad (3)$$

where Z is a geometric factor which depends on the relaxation process, ν is the attempt frequency, and ΔS_j is the activation entropy. For the special case of a single exponential relaxation

$$\Delta \equiv \frac{1}{\mu_i(t_2)} - \frac{1}{\mu_i(t_1)} = a_1 \left[\exp\left(\frac{-t_1}{\tau_1}\right) - \exp\left(\frac{-t_2}{\tau_1}\right) \right] \quad (4)$$

If it is assumed that the total relaxation strength, a_1 , is independent of temperature then the maximum of Δ with respect to temperature, Δ_{pk} , occurs at T_{pk} with a relaxation time

$$\tau_{pk} = \frac{t_2 - t_1}{\ln\left(\frac{t_2}{t_1}\right)}. \quad (5)$$

which for $t_1 = 1$ min and $t_2 = 5$ min, equals 149 sec.

In general a_1 is proportional to the concentration of the relaxing species and inversely proportional to the temperature. As will be shown in the discussion, in the case where the relaxing species is a cluster of n solute atoms and its binding enthalpy $E_b^{(n)}$ is small, the relaxation strength is given by

$$a_1 = \eta C^n T^{-1} \exp(E_b^{(n)}/RT) \quad (6)$$

where η is a constant which depends on the cluster geometry and C is the total solute concentration. Using equation (6) in the expression for Δ [equation (4)] in the limit of small $E_b^{(n)}$ leads to values of τ_{pk} which differ from those obtained from equation (5) by less than 2% in the temperature range of interest.

The relaxation enthalpy, Q and preexponential τ_0 can be obtained from the disaccommodation spectrum in the following manner. The relaxation time at the maximum of the disaccommodation curve, τ_{pk} , is given by equation (5). The relaxation time, $\tau_{1/2}$, at a temperature, $T_{1/2}$, which corresponds to $\Delta = 1/2\Delta_{pk}$ may be obtained from equations (4) and (6) if $E_b^{(n)}$ is known;

$$\begin{aligned} \left(\frac{T_{1/2}}{2T_{pk}}\right) \exp\left\{\frac{E_b^{(n)}}{R}\left(\frac{1}{T_{pk}} - \frac{1}{T_{1/2}}\right)\right\} \\ = \frac{\exp(-t_1/\tau_{1/2}) - \exp(-t_2/\tau_{1/2})}{\exp(-t_1/\tau_{pk}) - \exp(-t_2/\tau_{pk})} \end{aligned} \quad (7)$$

Knowing τ_{pk} and $\tau_{1/2}$ one can calculate Q and τ_0 in equation (2). The activation enthalpy is given by

$$Q = \frac{R \ln(\tau_{1/2}/\tau_{pk})}{\left[\frac{1}{T_{1/2}} - \frac{1}{T_{pk}}\right]} \quad (8)$$

The value of $E_b^{(n)}$ can be determined independently or by fitting equations (4) and (6) to the experimental Δ vs. T curve. As will be shown later the present results are probably due to Ti pair relaxations with $E_b^{(n)} \approx 0.17$ eV. Using this value, the Δ vs. T data was analyzed for τ_0 and Q with the results shown in Table 1. (The two sets of data indicate the ranges of Q and τ_0 which can be used to fit the experimental results.) The results obtained assuming a constant relaxation amplitude [$a_1 \neq f(T)$] are also given. The

TABLE 1. Single exponential analysis

$a = \frac{\eta C^2}{T} \exp \frac{E_b^{(2)}}{RT}$ $a \neq a(T)$							
wt. % Ti	at. % Ti	$\frac{Q}{\text{(mole)}}$	τ_0 (sec)	$\frac{Q}{\text{(mole)}}$	τ_0 (sec)	$\frac{Q}{\text{(mole)}}$	τ_0 (sec)
4.2	5.14	69.4	0.12×10^{-16}	65.5	1.6×10^{-16}	64.3	3.0×10^{-16}
2.5	3.06	68.4	0.17×10^{-16}	64.6	2.1×10^{-16}	65.5	1.0×10^{-16}
1.7	2.08	69.6	0.56×10^{-17}	65.6	0.8×10^{-16}	64.6	1.3×10^{-16}

fit of equation (4) [with a_1 given by equation (6)] to the data given in Fig. 7 is shown in Fig. 9. The high temperature background has been subtracted from the data. The analysis results in a slight increase in relaxation time with Ti concentration as will be discussed later. The value of Δ_{pk} is proportional to the total relaxation strength ($\Delta_{pk} = 0.533 a_1$ for $t_1 = 1$ min, $t_2 = 5$ min) as shown by equation (4). The relation between a_1 and the solute concentration, C , is given by equation (6). The experimentally observed maximum in the disaccommodation peaks on the first cooling cycle varied as the square of the Ti concentration (Fig. 10). The variation of relaxation

strength over the experimentally observed range of T_{pk} with composition (Fig. 9) is small [equation (6)] and is therefore neglected.

The small decrease in the peak height which was observed on the second cooling cycle (Fig. 8) was not accompanied by a change in Q or τ_0 . This suggests that the Ti solute concentration which contributed to the relaxation strength was decreased slightly by cycling through the transformation and by annealing at elevated temperatures. The extent of this decrease was small and may be estimated using Fig. 10.

3.3 Lognormal analysis

The isothermal relaxation curves were analyzed in terms of a single exponential relaxation process with a

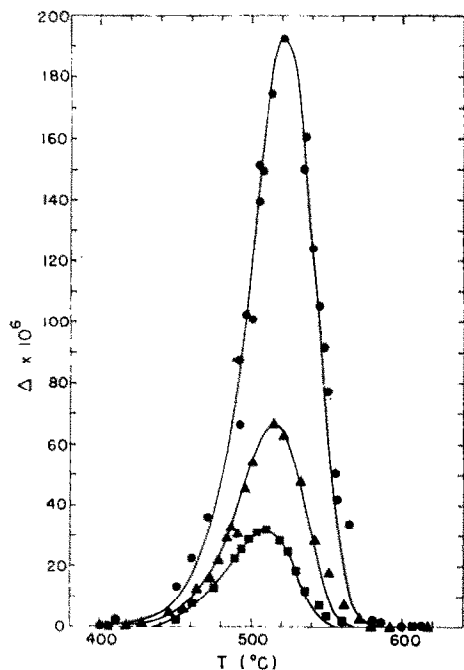


FIG. 9. Variation of relaxation strength with temperature (1st time down after 1/2 hr at 700°C *in situ*) for the 4.2 (●), 2.5 (▲), and 1.7 (■) wt. % Ti alloys. The curves are calculated using the single exponential relaxation analysis:

- $Q_{\bullet} = 69.4$ kcal/mole,
- $Q_{\blacktriangle} = 68.4$ kcal/mole, and
- $Q_{\blacksquare} = 69.6$ kcal/mole.

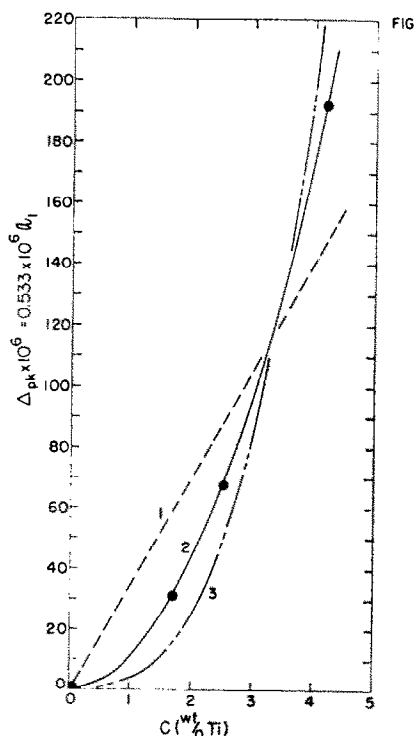


FIG. 10. Variation of relaxation strength with Ti concentration. The curves, linear, square, and cubic least squares fits to the data, show the excellent dependence of relaxation strength on the square of the Ti concentration.

lognormal distribution of relaxation times⁽²⁶⁾ using the equation:

$$\frac{1}{\mu_i(\infty)} - \frac{1}{\mu_i(t)} = \frac{1}{\mu_i(\infty)} - \frac{1}{\mu_i(0)}$$

$$= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \exp \left\{ -\mu^2 - \exp \left[\ln \left(\frac{t}{\tau_M} \right) - \beta \mu \right] \right\} d\mu \quad (9)$$

where β is the half-width of the Gaussian relaxation time distribution and τ_M is the most probable relaxation time.

During the measurement of μ_i vs. time at constant temperature it was observed that μ_i did not approach an asymptotic value, even after $100\tau_D$ in some cases (i.e., 100 relaxation times as determined from the previous analysis), which made determination of $\mu_i(\infty)$ difficult. (This long time variation of μ_i was associated with the high temperature history effects previously described and will be discussed later.) Two procedures used to establish $\mu_i(\infty)$ were to assume $\mu_i = \mu(\infty)$ at $10\tau_D$ and $20\tau_D$. In a third procedure it was determined that $(d\mu_i(1 \text{ min})/d\theta)$, where θ is the total time at temperature, was of the order of 10^{-6} sec^{-1} for the temperatures and compositions studied. The value of μ_i when $d\mu_i/dt \sim 10^{-6} \text{ sec}^{-1}$ was taken as $\mu_i(\infty)$. This usually corresponded to times greater than $20\tau_D$, the time decreasing with decreasing temperature. Analysis of the isothermal relaxation data using these three methods of determining $\mu_i(\infty)$ yielded similar results.

The most probable relaxation times, τ_M , as a function of $1/T$ are given in Fig. 11 for $t_\infty = 10\tau_D$. As for the previous analysis, the data for all Ti concentrations resulted in a single activation enthalpy of 69 kcal./mole, a τ_0 of 0.4×10^{-16} sec and a small apparent increase in τ_0 with increasing Ti concentration as shown in Table 2. The values of τ_M obtained increased slightly as the time, t_∞ , at which $\mu_i = \mu_i(\infty)$ was increased. The half-width of the Gaussian relaxation time distribution, β , was essentially independent of temperature for $t_\infty = 10\tau_D$ and had

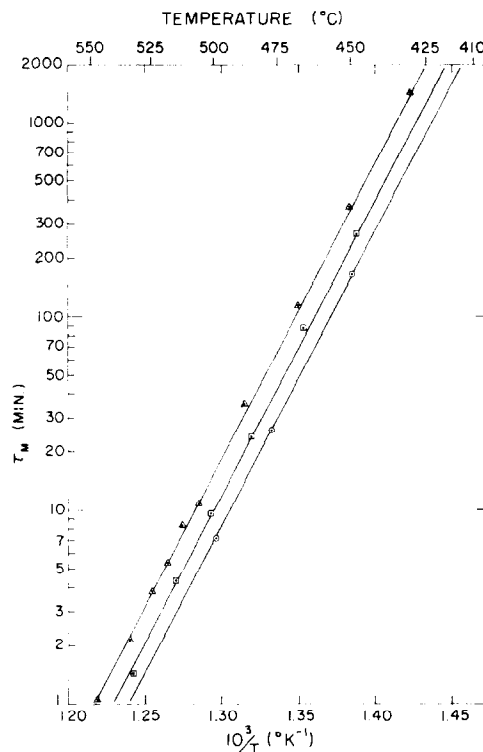


FIG. 11. Semi-logarithmic plot of the most probable relaxation time (as derived from the lognormal analysis) vs. $1/T$ for the 4.2 (Δ), 2.5 (\square), and 1.7 (\circ) Ti alloy relaxations terminated at $t_\infty = 10\tau_D$.

$$Q = 69 \text{ kcal/mole}$$

$$\tau_0 = 0.66 \times 10^{-16} \text{ sec; 4.2\% Ti}$$

$$\tau_0 = 0.42 \times 10^{-16} \text{ sec; 2.5\% Ti}$$

$$\tau_0 = 0.30 \times 10^{-16} \text{ sec; 1.7\% Ti}$$

the values 1.25 (4.2 wt.% Ti), 1.15 (2.5 wt.% Ti), and 0.92 (1.7 wt.% Ti). The fit of the normalized experimental permeability data to the lognormal analysis for $t_\infty = 10\tau_\infty$ is shown in Fig. 12.

3.4 Sum of exponential analysis

The isothermal permeability data were analyzed as a sum of relaxation processes using the relation

$$\frac{1}{\mu_i(\infty)} - \frac{1}{\mu_i(t)} = \sum_j a_j \exp \left(\frac{-t}{\tau_j} \right) \quad (1)$$

where

$$\sum_j a_j = \frac{1}{\mu_i(\infty)} - \frac{1}{\mu_i(0)} \quad (10)$$

TABLE 2. Results of analysis of isothermal relaxation data

wt. % Ti	Lognormal		Sum of exponentials		Single exponential	
	τ_0 (sec)	Q (kcal/mole)	τ_0 (sec)	Q (kcal/mole)	τ_0 (sec)	Q (kcal/mole)
4.2	0.66×10^{-16}	69	0.66×10^{-16}	69	0.6×10^{-16}	69
2.5	0.42×10^{-16}	69	0.40×10^{-16}	69	0.35×10^{-16}	69
1.7	0.3×10^{-16}	69	0.27×10^{-16}	69	0.23×10^{-16}	69

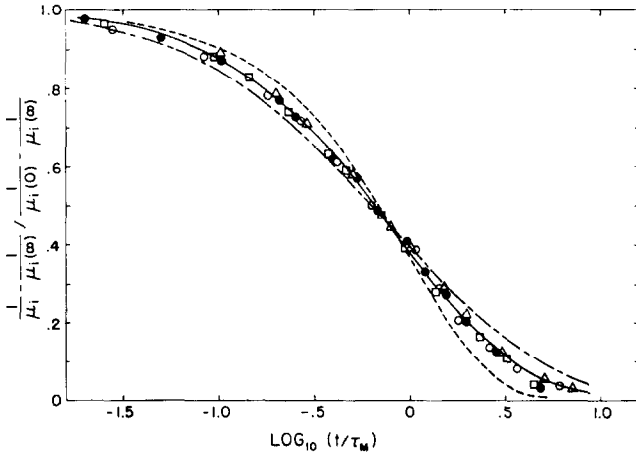


FIG. 12. Normalized isothermal relaxation of the initial permeability terminated at $t_{\infty} = 10\tau_D$ for 506.8°C (●), 524.2°C (○), 533.2°C (□), and 545.7°C (△) for the 4.2 wt.% Ti alloy. The curves are calculated from the lognormal analysis using β 's of 0 (---), 1.25 (—), and 1.75 (- - -).

The relative relaxation strengths A_j are defined such that

$$A_j = \frac{a_j}{\sum_j a_j} \quad (11)$$

The experimental values of $1/\mu_i(\infty) - 1/\mu_i(t)$ were analyzed as a sum of "j" relaxations by successive subtraction of the contribution of the process having the longest relaxation time from the measured data plotted as $\ln[1/\mu_i(\infty) - 1/\mu_i(t)]$ vs. t . The analysis was performed by a computer program which allowed the number of relaxations, the relaxation strengths, and the relaxation times to be adjusted to obtain a "best" least squares fit. The results of these analyses are shown in Figs. 13-15 where the relaxation times are plotted as a function of the inverse absolute temperature. The relative relaxation strengths A_j are indicated for each point. For this analysis t_{∞} was taken as $10\tau_D$. The least squares analysis required only two exponentials over the entire temperature range. For the temperatures examined a major part

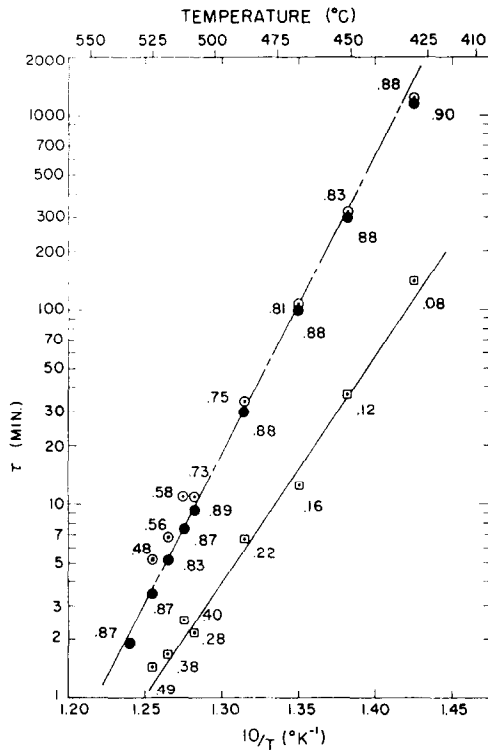


FIG. 13. Semi-logarithmic plot of relaxation times (as derived from the sum of exponential analysis) vs. $1/T$ for the 4.2 wt.% Ti alloy relaxations terminated at $t_{\infty} = 10\tau_D$. The number of terms in the sum was (a) allowed to vary to obtain the best fit to the data (○ and □) and (b) set equal to "one" to analyze the data as a single exponential relaxation (●). The numbers refer to the relative amplitudes attributable to the respective relaxations. The curve --- is the τ_M vs. $1/T$ data obtained from the lognormal analysis and has an activation enthalpy $Q = 69$ kcal/mole.

$$Q_{\circ} = Q_{\bullet} = 69 \text{ kcal/mole.}$$

$$Q_{\square} = 54 \text{ cal/mole.}$$

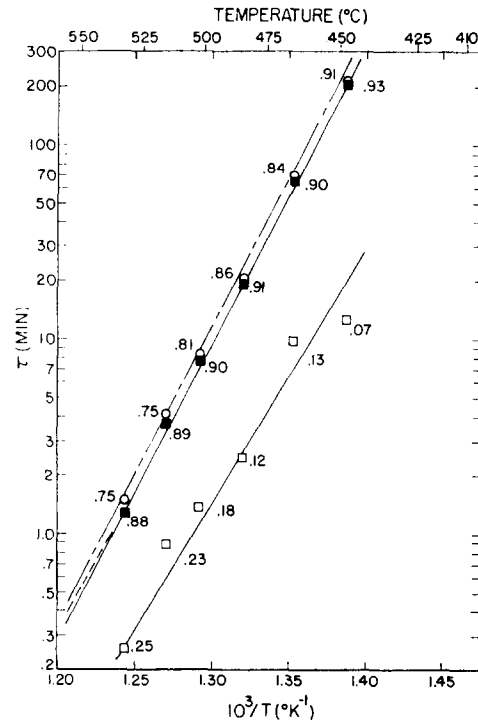


FIG. 14. Semi-logarithmic plot of relaxation times (as derived from the sum of exponential analysis) vs. $1/T$ for the 2.5 wt.% Ti alloy relaxations terminated at $t_{\infty} = 10\tau_D$. The number of terms in the sum was (a) allowed to vary to obtain the best fit to the data (○ and □), and (b) set equal to "one" to analyze the data as a single exponential relaxation (□). The numbers refer to the relative amplitudes attributable to the respective relaxations. The curve --- is the τ_M vs. $1/T$ data obtained from the lognormal analysis and has an activation enthalpy, $Q = 69$ kcal/mole.

$$Q_{\circ} = Q_{\blacksquare} = 69 \text{ kcal/mole.}$$

$$Q_{\square} = 60 \text{ kcal/mole.}$$

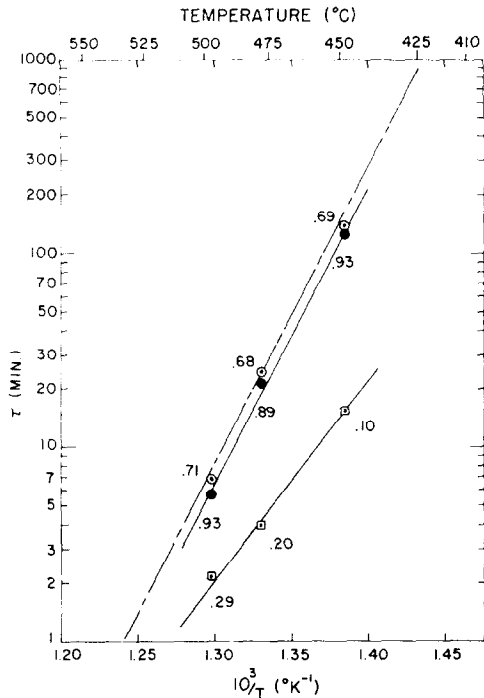


FIG. 15. Semi-logarithmic plot of relaxation times (as derived from the sum of exponential analysis) vs. $1/T$ for the 1.7 wt. % Ti alloy relaxations terminated at $t_{\infty} = 10 \tau_p$. The number of terms in the sum was (a) allowed to vary to obtain the best fit to the data (\circ and \square), and (b) set equal to "one" to analyze the data as a single exponential relaxation (\bullet). The numbers refer to the relative amplitudes attributable to the respective relaxations. The curve ---- is the τ_M vs. $1/T$ data obtained from the lognormal analysis and has an activation enthalpy, $Q = 69$ kcal/mole.

$$Q_{\circ} = Q_{\bullet} = 69 \text{ kcal/mole.}$$

$$Q_{\square} = 47 \text{ kcal/mole.}$$

of the total relaxation strength was associated with the component having the longer relaxation times which had a $Q = 69$ kcal/mole and $\tau_0 \sim 0.4 \times 10^{-16}$ sec as shown in Table 2. These values agreed very well with those obtained from the lognormal analysis. The second relaxation component was characterized by $Q = 54 \pm 8$ kcal/mole and $6 \times 10^{-12} \text{ sec} \geq \tau_0 \geq 10^{-15} \text{ sec}$.

The data were also analyzed using a least squares fit to a single exponential relaxation and the results are shown in Figs. 13-15 and in Table 2. Approximately 90% of the total relaxation strength could be accounted for by a single relaxation whose relaxation times agreed well with those of the lognormal analysis. The comparison of the calculated single relaxation curves with the experimental data is shown in Fig. 16 for the typical data on the 2.5 wt. % Ti alloy. In this case the amplitude and relaxation time of the single relaxation were both allowed to vary to obtain the best least squares fit. As expected the major discrepancies are observed at short relaxation times again indicating the necessity for a second exponential relaxation.

It was previously shown that the relaxation strength obtained from the analysis discussed in Section 3.2 varied as the square of the titanium concentration. The total relaxation strength obtained from the isothermal data,

$$a_1 = \frac{1}{\mu_i(t_{\infty})} - \frac{1}{\mu_i(t=0)} \quad (12)$$

has the same magnitude and also exhibits a dependence

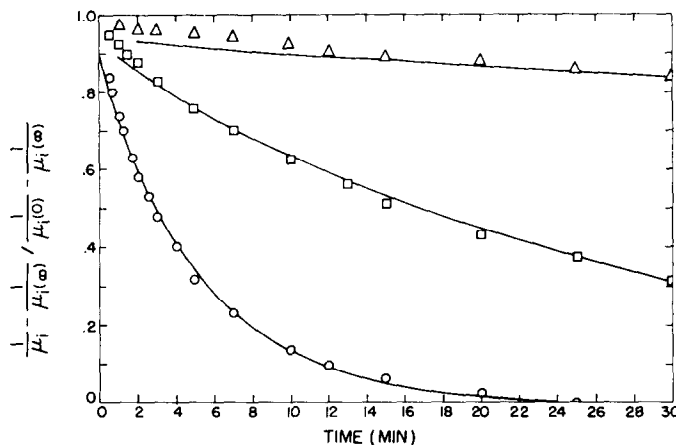


Fig. 16. Isothermal relaxation of the normalized initial permeability terminated at $t_{\infty} = 10 \tau_p$ at several temperatures for the 2.5 wt. % Ti alloy. The curves are calculated from the sum of exponential analysis using a single exponential relaxation.

$$T = 448^{\circ}\text{C}, \tau = 206 \text{ min}, A = 0.93 (\triangle)$$

$$T = 485^{\circ}\text{C}, \tau = 19.6 \text{ min}, A = 0.91 (\square)$$

$$T = 514^{\circ}\text{C}, \tau = 3.6 \text{ min}, A = 0.90 (\circ)$$

on the square of the titanium concentration (Fig. 17) for $t_{\infty} = 10\tau_D$. The value of a_1 exhibited the temperature dependence expected from equation (6) as will be discussed shortly.

3.5 Metallography of Co-Ti alloys

A detailed metallographic study of the alloys was carried out (a) in the as-cast condition, (b) after heating to 700°C, annealing for 30 min and slow cooling for the disaccommodation spectrum, and (c) after a second heating to 700°C, annealing for 30 min again and slow cooling for the isothermal relaxation measurements. Quantitative X-ray microprobe analyses of these specimens were carried out by Dr. D. Beaman at the Dow Chemical Company. The Co-4.2% Ti alloy in the as-cast condition showed a significant amount of Ti rich precipitates as shown in the photomicrograph in Fig. 18 and the accompanying X-ray integrated intensity photograph. After the first heating and cooling cycle the precipitates were no longer present and the inhomogeneity in Ti content was significantly reduced (Fig. 19). Probe analysis for cobalt and oxygen showed essentially no inhomogeneity in the distribution of these elements. The results of quantitative X-ray microprobe scans for Ti and Co across a precipitate in the as-cast Co-4.2 wt.% Ti alloy showed the precipitate to be 87 wt.% Co and

13 wt.% Ti. This agrees very well with the composition of the γ phase in the Co-Ti phase diagram as recently determined by Fountain and Forgeng.⁽²³⁾ The observed decrease in inhomogeneity with time at temperature is in disagreement with the observation of Fountain *et al.*^(23,27) that at this composition the γ phase tended to precipitate from solid solution with time at temperature. The present results suggest a solid solubility at 700°C which is larger than that reported by Fountain and Forgeng. In a 5.2 wt.% Ti alloy the precipitates did not dissolve during the annealing heat treatments at 700°C which suggests that the maximum solid solubility of Ti in Co at 700°C is between 4.2 and 5.2 wt.% Ti in contrast to Fountain and Forgeng's value of less than 3 wt.% Ti.

The effect of homogenization on the high temperature disaccommodation was determined by measuring the value of β (the half-width of the Gaussian relaxation time distribution in the lognormal analysis) after various heat treatments. These results suggest that high temperature annealing affects the relaxation contribution due to a process which has a very long relaxation time and contributes to the long time "tail" observed for the isothermal disaccommodations. The metallographic observations suggest that this long relaxation time process is associated with long range diffusion and homogenization of Ti. The disaccommodation peak is unaffected by the homogenization except for a small change in the value of Δ_{pk} .

4. DISCUSSION

The salient experimental observations concerning the temperature dependent disaccommodation may be summarized as follows:

1. The disaccommodation observed in the alloy specimens in the temperature range 400–700°C was not found in pure cobalt (see Appendix).
2. The relaxation times exhibit temperature dependences characteristic of thermally activated processes.
3. The activation enthalpy (Q) appears to be independent of composition and equal to 69 ± 1 kcal/mole; τ_0 is of the order of 10^{-16} sec.
4. The relaxation strength, a_1 , varies as the square of the titanium concentration.
5. The observed disaccommodation can be described predominantly by a single first order relaxation process.

The dependence of the observed disaccommodation on the square of the titanium concentration, including the absence of the disaccommodation in pure cobalt

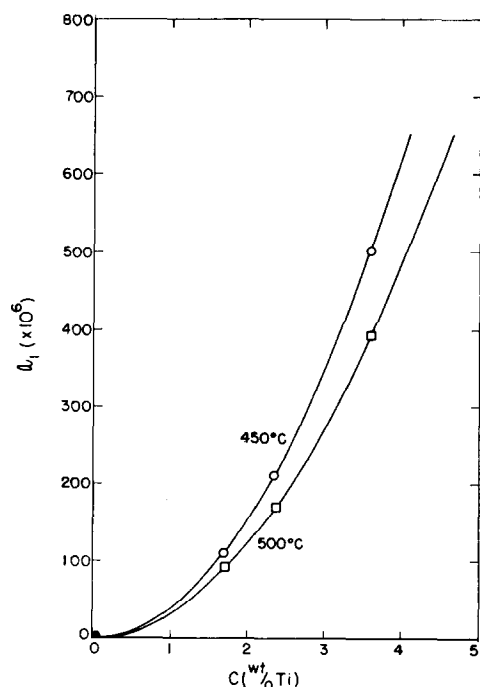


Fig. 17. Variation of the total relaxation strength (for $t_{\infty} = 10\tau_D$) with effective titanium concentration. The curves are least square fits to the data showing the parabolic dependence of total relaxation strength on Ti concentration at (○) 450°C and (□) 500°C.

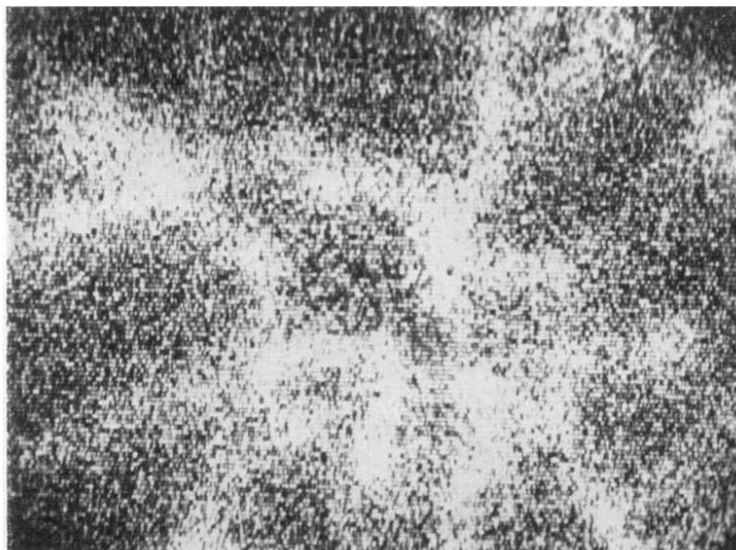
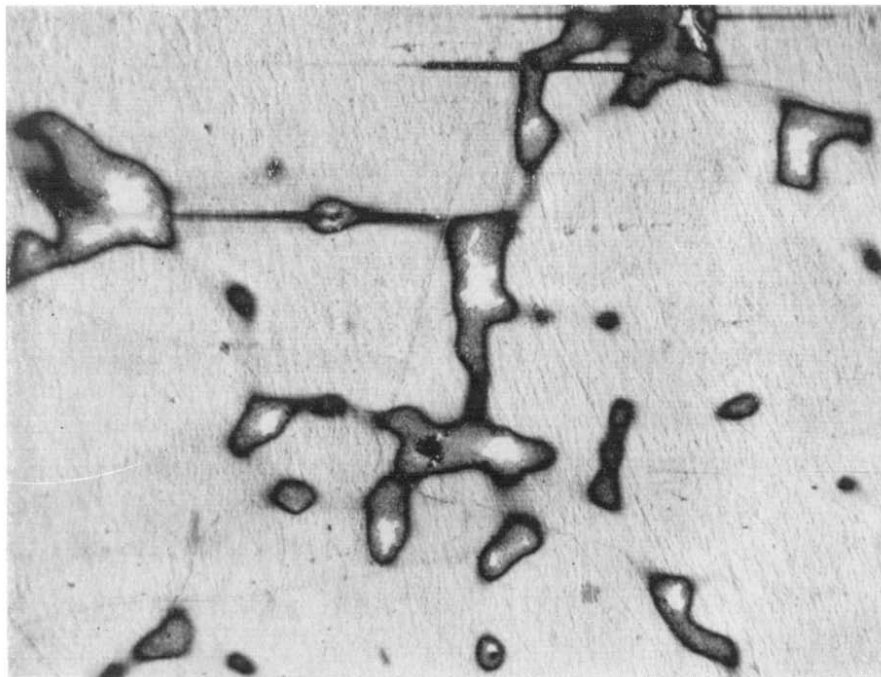


FIG. 18. As-cast Co-4.2 wt. % Ti alloy (10 acetic, 10 H₂O, 10 HNO₃, 40 HCl etch) \times 250, with X-ray integrated intensity microprobe analysis for Ti of the area shown in the photograph.

(see Appendix), suggests that the disaccommodation is due predominantly to the reorientation of Ti atom pairs. If this assignment is in fact correct the relaxation behavior should satisfy at least 2 criteria:

1. The relaxation time, τ , should be insensitive to the Ti concentration for compositions where the solute pairs are sufficiently far apart.
2. The law of mass action should hold for the equilibrium number of Ti pairs for a given total Ti concentration.

The experimental results (Fig. 11 and Tables 1 and 2) lead to the conclusion that in the composition range examined the relaxation time τ is a constant to within a factor of two. As seen in Fig. 11 there is however a small temperature independent monotonic increase of τ as the concentration of titanium is increased. A similar effect is shown on comparing the relaxation times of Figs. 13-15. Analysis of the data of Fig. 11 shows that if Q is chosen as constant for all compositions, τ_0 , appears to increase by about a

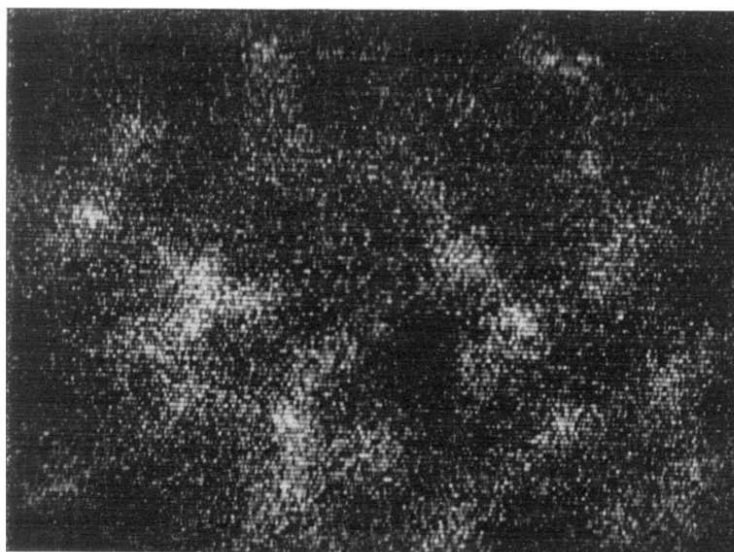
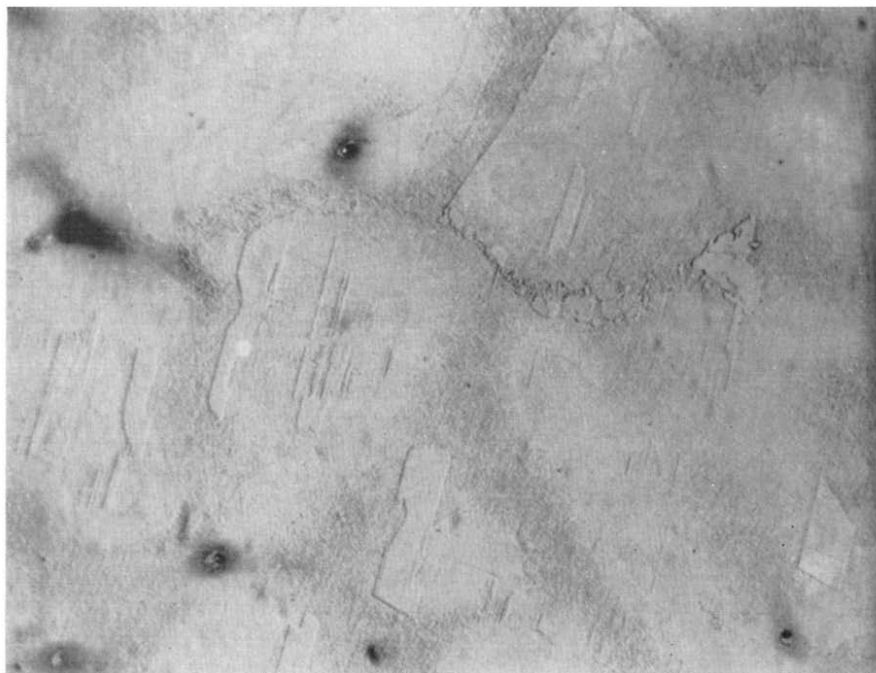


FIG. 19. Co-4.2 wt.% Ti alloy after measurement (10 acetic, 10 H₂O, 10 HNO₃, 40 HCl etch) $\times 250$, with X-ray integrated intensity microprobe analysis for Ti of the area shown in the photograph.

factor of 2 from the 1.7% Ti alloy to the 4.2% Ti alloy. Alternatively, within the precision of the data one could allow Q to vary by 1 part in 70 (e.g., Q (1.7% Ti) = 68 kcal/mole and Q (4.2% Ti) = 69 kcal/mole) and obtain a constant value of τ_0 . The small dependence of τ on C_{Ti} may result from the interaction between solute atom pairs. Even in the dilute alloy (~ 2 at.% Ti) the mean distance between a solute pair and an adjacent solute atom is only of the order of 5 Å. In view of the above, the first criterion would appear to be satisfied.

The values of the relaxation times, τ , at each temperature may be converted to diffusion coefficients using the relations

$$\tau_0 = \nu^{-1} \exp\left(-\frac{\Delta S}{R}\right) \quad (3)$$

$$D_0 = \frac{b^2}{6} \nu \exp\left(\frac{\Delta S}{R}\right) \quad (13)$$

and

$$D = D_0 \exp\left(\frac{-Q}{RT}\right). \quad (14)$$

The range of experimentally observed τ_0 corresponds to $0.7 \leq D_0 \leq 37$. For $\tau_0 = 0.6 \times 10^{-16}$ one obtains

$$D = 3.5 \exp\left(\frac{-69 \text{ kcal/mole}}{RT}\right) \text{ cm}^2/\text{sec.} \quad (15)$$

Using $\nu = 10^{13} \text{ sec}^{-1}$ and $3 \times 10^{-16} \text{ sec} \geq \tau_0 \geq 0.56 \times 10^{-17} \text{ sec}$ leads to $5.8 R \leq S \leq 7.5 R$. This rather high activation entropy suggests that the reorientation requires highly correlated atom movements and that the relaxing defect is not as simple as a nearest neighbor pair.

If the law of mass action applies and if equilibrium exists between titanium atoms in single and pair configurations, then, neglecting higher order clusters, the concentration of pairs, C_2 , should be related to the concentration of singles, C_1 , and the total concentration, C , according to the approximate expressions;

$$C_2 = ZC_1^2 \exp\left(\frac{-\Delta S_f^{(2)}}{R}\right) \exp\left(\frac{E_b^{(2)}}{RT}\right) \quad (16)$$

and

$$C = C_1 + 2C_2 \quad (17)$$

where Z is a geometrical constant giving the number of orientations of pairs which are possible about a given lattice site, $E_b^{(2)}$ is the enthalpy of formation of pairs from singles, $\Delta S_f^{(2)}$ is the entropy of formation of pairs, and R and T have their usual meaning. The assumption of an ideal solution is made in order to use concentrations rather than activities in equation (16). If the binding enthalpy $E_b^{(2)}$ is small, then $C_2 \ll C_1$ and $C \approx C_1$. Substituting into equation (16) yields

$$C_2 = ZC^2 \exp\left(\frac{-\Delta S_f^{(2)}}{R}\right) \exp\left(\frac{E_b^{(2)}}{RT}\right). \quad (18)$$

The relaxation strength;

$$a_1 = \frac{1}{\mu_i(\infty)} - \frac{1}{\mu_i(0)} \quad (12)$$

is expected to be proportional to the concentration of the relaxing species in the case of dilute solutions. In the present study;

$$a_1 = KC_2 \quad (19)$$

where K is the relaxation strength of Ti atom pairs per unit concentration in cobalt. Hence, if $\Delta S_f^{(2)}$ and $E_b^{(2)}$ are independent of concentration, then at a given temperature a_1 should be proportional to the square of the Ti concentration as experimentally observed (Fig. 17).

In the limit of dilute solutions, both the theories of Zener^(2,3) and of LeClaire and Lomer⁽⁴⁾ result in

$$a_1 = k \frac{C_2}{T} \quad (20)$$

where the proportionality constant, k , differs for the two theories. Using equation (20), one may write equation (18) in the form

$$\ln(a_1 T) = \left[\ln(kZC^2) - \frac{\Delta S_f^{(2)}}{R} \right] + \frac{E_b^{(2)}}{RT} \quad (21)$$

Since k and $\Delta S_f^{(2)}$ are not strong functions of temperature, a plot of $\ln(a_1 T)$ vs. $1/T$ yields $E_b^{(2)}$. As shown in Fig. 20, the data appear to be described by equation (21) and yield $E_b^{(2)} = 0.17 \pm 0.08 \text{ eV}$.

In addition to the disaccommodation caused by Ti atom pair reorientation the data indicate that other types of relaxation processes may be observed in the Co-Ti system. These may be caused by long range diffusion of solute atoms over distances comparable to the Bloch wall thickness or by a thermally activated motion of the Bloch walls.⁽²⁴⁾ The Ti pair reorientation was observed in the temperature range 430–530°C. In this temperature range one cannot expect a large contribution due to long range diffusion of the solute atoms since the reorientation of Ti pairs is accomplished by a small number of jumps per solute atom and should be observable at temperatures below those at which long range migration of solute atoms

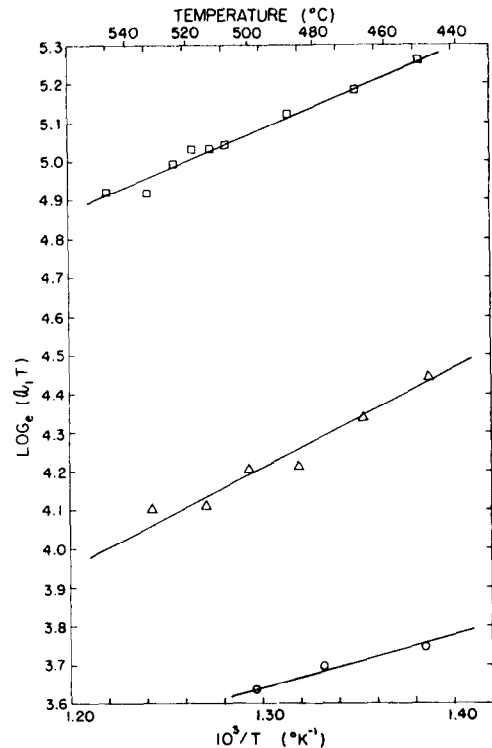


Fig. 20. Determination of the binding energy of Ti pairs ($E_b^{(2)}$) in dilute f.c.c. cobalt base alloys. $\tau_\infty = 10\tau_D$.

4.2 wt.% Ti, $E_b^{(2)} = 0.18 \text{ eV}$ (\square);

2.5 wt.% Ti, $E_b^{(2)} = 0.22 \text{ eV}$ (\triangle);

1.7 wt.% Ti, $E_b^{(2)} = 0.12 \text{ eV}$ (\circ).

can occur. The increase in the magnitude of the disaccommodation background, $1/\mu_i$ (5 min) - $1/\mu_i$ (1 min), observed in the temperature range 600-700°C with successive cooling cycles after heating and annealing at 700°C (Fig. 8) is believed to be due to long range diffusion of Ti atoms. This assertion is supported by the metallographic observations discussed earlier which showed solution of precipitates and homogenization of the alloy with time at temperature in the range 600-700°C. The observed decrease in the magnitude of the initial permeability during the first cooling cycle as compared with the first heating cycle (Fig. 3) was largest for the most concentrated alloy and was monotonically smaller the more dilute the alloy. The decrease correlated well with the observed concentration dependence of μ_i (Fig. 5) and is therefore attributed to solution of precipitates and/or homogenization of the alloys. The solution of precipitates results in a small increase in the mean Ti concentration contributing to the relaxation and therefore in the increase in the disaccommodation for the Ti pair reorientation on annealing at 700°C which was observed. That the Ti pair reorientation peak height is always smaller during the heating than the cooling cycle is attributable to the unavoidable introduction of strain due to the h.c.p. \rightarrow f.c.c. transformation which masks the reorientation peak. The strain appears to anneal out in 1/2 hr at 700°C.

Long range diffusion also accounts for the observed decrease in peak height (measured on cooling) of the Ti pair reorientation with successive cycles through the transformation (Fig. 8). Each time one goes through the h.c.p. \rightarrow f.c.c. transformation more dislocations are generated resulting in an increasingly sluggish transformation (Appendix). The decrease in the height of the pair reorientation peak resulting from a decrease in effective Ti concentration with no attendant Ti precipitation suggests that some Ti has migrated to and become bound by dislocations. These small changes in effective Ti concentration do not change the Q and τ_0 values characterizing the Zener disaccommodation.

In addition to the Ti pair reorientation peak a second disaccommodation maximum was observed at about 620°C on the first heating after each cycle through the h.c.p. \rightarrow f.c.c. transformation. This disaccommodation effect was removed by a 1/2 hr anneal at 700°C. The apparent peak at about 620°C is accompanied by a precipitous decrease in μ_i with time at temperature and is believed to be due to annealing effects rather than to a relaxation process. A peak in the reluctivity difference due to annealing could arise if two competing effects such as long range diffusion of

solute atoms and polygonization of dislocations produced by the transformation are operative. Such a peak would not be observed on cooling since the annealing is irreversible. However, on going through the transformation new dislocations are formed and the annealing effects should be seen again as is observed.

5. CONCLUSIONS

Measurements of the magnetic disaccommodation in cobalt base alloys containing 0 to 4.2 wt.% titanium showed a strong temperature dependence of the disaccommodation in the range 430-530°C. Analysis of the data in terms of (a) a single exponential relaxation, (b) a single relaxation process with a lognormal distribution of relaxation times, and (c) a sum of exponential relaxations all resulted in the conclusion that the disaccommodation could be accounted for by a single predominant process. The relaxation strength varied as the square of the titanium concentration and was characterized by an activation enthalpy of 69 ± 1 kcal/mole and a τ_0 of the order of 10^{-16} sec. The disaccommodation was attributed to the reorientation of substitutional solute atom (Ti) pairs. From the temperature dependence of the relaxation strength the binding energy of Ti atom pairs was determined to be 0.17 ± 0.08 eV.

Other magnetic effects observed in the temperature range 600-700°C were accounted for on the basis of long range diffusion of Ti atoms to dislocations generated during the transformation.

ACKNOWLEDGMENTS

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APPENDIX

Magnetic Studies in Pure Cobalt

Johnson Matthey Co. cobalt rods (99.998% pure) 5 mm dia. and 2 in. long were annealed at 1000°C for 3 days in a static vacuum of better than 10^{-6} torr. The variation of the initial permeability, μ_i , at 1 min after demagnetization is shown in Fig. 21 on heating and cooling between 400°C and 700°C. The disaccommodation $1/\mu_i(5 \text{ min}) - 1/\mu_i(1 \text{ min})$ for the

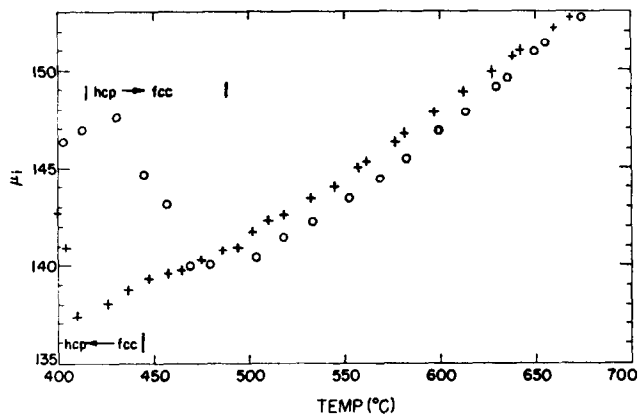


FIG. 21. Initial permeability at 1 min after demagnetization as a function of temperature for the pure cobalt specimen on heating (○) and cooling (+).

same temperature interval is shown in Fig. 22. The increase of the permeability μ_i at a fixed time after demagnetization on annealing at elevated temperatures may be due to the annealing out of the defects introduced by the h.c.p. \rightarrow f.c.c. transformation. The hysteresis in the phase transformation in pure cobalt on heating and cooling was less than in the alloys and the temperature range over which the transformation occurred was larger. On heating, the h.c.p. \rightarrow f.c.c. transformation occurred between about 415 and 490°C. On cooling, the f.c.c. \rightarrow h.c.p. transformation began at about 450°C (whereas in the alloys it always began below 400°C and was therefore never observed). The shaded regions in Fig. 22 denote temperature intervals in which the disaccommodation [defined by $1/\mu_i(5) - 1/\mu_i(1)$] was negative due to the unusual shape of the relaxation curves in the presence of varying amounts of h.c.p. and f.c.c. cobalt. On repeated cycling through the transformation, μ_i decreased but exhibited the same temperature dependence. This may be the result of transformation-introduced defects on the initial permeability. Cycling between 450 and 550°C after a 1/2 hr anneal at 700°C and without allowing the phase transformation to occur resulted in completely reproducible μ_i values.

The magnitude of the disaccommodation $1/\mu_i(5 \text{ min}) - 1/\mu_i(1 \text{ min})$ showed a small monotonic decrease with increasing temperature between the temperature of the phase transformation and 640°C, a minimum at about 640°C, and an increase above this temperature. At high temperatures (above about 520°C) the disaccommodation is larger after the 700°C anneal. For pure cobalt no maximum in the disaccommodation was observed in the temperature range (about 520°C) which would correspond to the effects noted in the cobalt-titanium alloys.

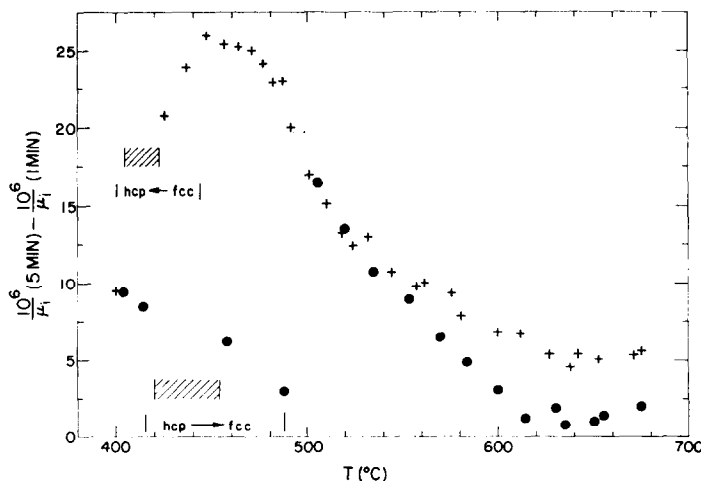


FIG. 22. Variation of relativity difference with temperature for the pure cobalt specimen on heating (●) and cooling (+).