The Growth of Gamma Prime Precipitates in Aged Ni-Ti Alloys

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The kinetics of growth of the γ' precipitate in a Ni-8.74 wt pct Ti alloy were studied by magnetic analysis and transmission electron microscopy. The variation of the titanium content of the nickel-rich matrix as a function of aging time was studied by measuring the ferromagnetic Curie temperature of alloys aged at 692°, 593°, and 525°C. The kinetics of this process accurately obeyed the predictions of the Lifshitz-Wagner theory of diffusion controlled coarsening after relatively short aging times at all aging temperatures. Dark-field transmission electron microscopy was used to measure the particle-size distributions and the average particle sizes of samples aged for various times at 692°C. The kinetics of particle growth also obeyed the time law predicted by the Lifshitz-Wagner theory within the limits of experimental error. Additional analysis of the data provided a value of approximately 21 erg per sq cm for the interfacial free energy of the γ'-matrix interface, and a value for the diffusion coefficient of titanium in nickel which is in very good agreement with an independently determined value. The distribution of γ' particle sizes was found to be significantly broader than the theoretical distribution of the Lifshitz-Wagner theory. It is suggested that this is due to the relatively large lattice parameter mismatch between γ' and the Ni-Ti matrix. The results and conclusions of this study are critically compared with those of other investigations.

THE precipitation processes in aged nickel-based titanium alloys have been the subject of many investigations.[1-5] The earlier studies[1,2] showed that the stable hexagonal η phase (Ni_3Ti) was preceded by the metastable γ' precipitate, which also has the stoichiometry Ni_3Ti but possesses the Cu_3Au (Ll_2) crystal structure. It was also shown[1,2] that the γ' particles are fully coherent with the nickel-rich matrix, are cubic in shape with interfaces parallel to $\{100\}$, and tend to line up along $\langle 100\rangle$ producing the so-called "modulated" structure. In many respects γ' in Ni-Ti alloys behaves much like γ' in Ni-Al alloys (Ni_3Al, Ll_2 crystal structure), which is not too surprising because the two systems are structurally similar. In Ni-Al alloys the γ' precipitate grows by diffusion-controlled coarsening almost from the very beginning of aging at temperatures above 625°C,[6-8] but there is considerable confusion regarding the growth mechanism of γ' in Ni-Ti alloys. Ben Israel and Fine[3] and Dawance *et al.*[4] by a combination of magnetic analysis and deformation experiments, and Sass and Cohen[5] by transmission electron microscopy studies, have arrived at the conclusion that γ' in Ni-Ti alloys is itself preceded by another metastable precipitate with a composition approximating to Ni_6Ti. However, the data of Ben Israel and Fine have been analyzed with moderate success[9] according to the equations of the Lifshitz-Wagner[10,11] theory of diffusion-controlled coarsening. Significantly, the coarsening analysis[9] was relevant to the particular aging times during which Ni_6Ti was supposed to be transforming to γ'. Since the simultaneous occurrence of these two processes, *i.e.*, γ' coarsening and the transformation of Ni_6Ti to γ', over a prolonged period of aging is highly unlikely, this investigation was initiated with the intention of reconciling the disagreement about the interpretation of Ben Israel and Fine's kinetic data.

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EXPERIMENTAL PROCEDURES

General Principles. Two experimental techniques were used to follow the growth of γ': a) Magnetic analysis, to measure the ferromagnetic Curie temperature, θ_c, of the aged samples; b) Transmission electron microscopy, to measure the γ' particle size distributions and average particle sizes as functions of aging time.

The measurements of θ_c provide a sensitive measure of the manner in which the titanium content of the nickel-rich matrix changes as aging proceeds. In principle all that is required is an accurate calibration curve describing the dependence of θ_c on the titanium content of binary Ni-Ti solid solutions. The θ_c value of the aged sample can then be referred to the calibration curve to obtain the titanium content of the matrix. The γ' precipitates are not ferromagnetic[3] and therefore do not affect the measured value of θ_c. The technique owes its high sensitivity to the fact that θ_c is a very strong function of the titanium concentration of Ni-Ti solid solutions, as has been shown by several investigators.[3,12-14]

Measurements of the γ' particle sizes are readily accomplished by the technique of dark-field electron microscopy, wherein a superlattice reflection from the ordered γ' precipitates is used to form an image. The images thus formed are uncomplicated by the presence of coherency strain-field contrast[15] which appears in bright-field images when there is sufficient mismatch between the lattice parameters of the matrix and the precipitates.

Alloy Preparation, Fabrication, and Measurements. Ni-Ti alloys containing 2, 4, 6, 8, 8.74, and 10 wt pct Ti were prepared from high purity Johnson-Mathey nickel (37 ppm impurities) and iodide titanium. The alloys were induction melted in a water-cooled silver crucible under a static atmosphere of titanium-gettered argon, remelted twice in the same apparatus, and checked for weight losses which were found to be negligible. The alloys were then cold swaged to rod, 0.100 in. in diam, and homogenized for about 2 hr at 1000°C in a static titanium-gettered helium atmosphere. Most of the alloys were prepared for the purpose of establishing a calibration curve of θ_c vs wt fraction Ti, and were rolled to sheet ranging in thickness from 0.005 to 0.009 in. The 8.74 wt pct Ti alloy, selected for the aging experiments, was also rolled to rod form with a square cross-section of about 1 by 1 mm.

The Curie temperatures were measured by the induction method. No attempt was made to measure the magnitude of the ac magnetic field applied to the induction coils, but the field amplitude was kept constant for all the measurements and the frequency was maintained at 1000 Hz. All other procedures were identical to those used in the study of the coarsening of γ' in Ni-Al alloys.[8]

For the electron microscopy studies, disks 2.3 mm in diam were spark-machined from the sheet specimens, electrolytically jet-profiled, and prepared for final examination by electropolishing (at 8 to 10 v) in a solution of 30 pct nitric acid-70 pct methanol, cooled between −30° and −60°C. The thin foils were examined in a Siemens Elmiskop I, operating at an accelerating voltage of 100 kv.

Preliminary studies showed that the Ni-Ti alloys had a great tendency to oxidize. The reactivity of the Ni-Ti alloys caused certain difficulties which were never entirely eliminated, but which were satisfactorily overcome by the adoption of special procedures. Solution treatment and homogenization anneals were carried out in a vertical tube furnace with an atmosphere chamber so designed that the specimens could be introduced into the hot-zone of the furnace while under the protection of a titanium-gettered helium atmosphere. Before the specimens were introduced, the entire chamber was evacuated by a mechanical vacuum pump, flushed with helium, evacuated again and filled with helium to a slight negative pressure. The specimens were then lowered into the hot-zone and annealed in the static helium atmosphere. The helium flow was resumed prior to opening the bottom of the chamber for quenching.

Calibration Curve Determination. Small samples of cold-rolled sheet were given individual recrystallization and solutionizing treatments for 5 min at 1000°C, except for the 10 wt pct Ti alloy which was solution treated at 1050°C. The specimens, which were freely suspended by a wire, were then quenched into a brine solution refrigerated to about −11°C. The thin oxide scale on the calibration specimens was easily removed by electropolishing prior to making measurements.

The calibration curve is shown in Fig. 1, where the results of previous investigations[3,12-14] are shown for comparison. At values of w_{Ti} greater than approximately 0.02, θ_c is linearly related to w_{Ti} over the entire range of titanium concentrations encountered in this study. The Curie temperatures from this investigation are generally lower than those from the earlier studies by Marian[12] and Taylor and Floyd,[13] in fair agreement with those of Ben Israel and Fine, and in very good agreement with those of Stover and Wulff.[14]

For the purpose of evaluating w_{Ti} from measurements of θ_c, the data were fitted to the following empirical equation:

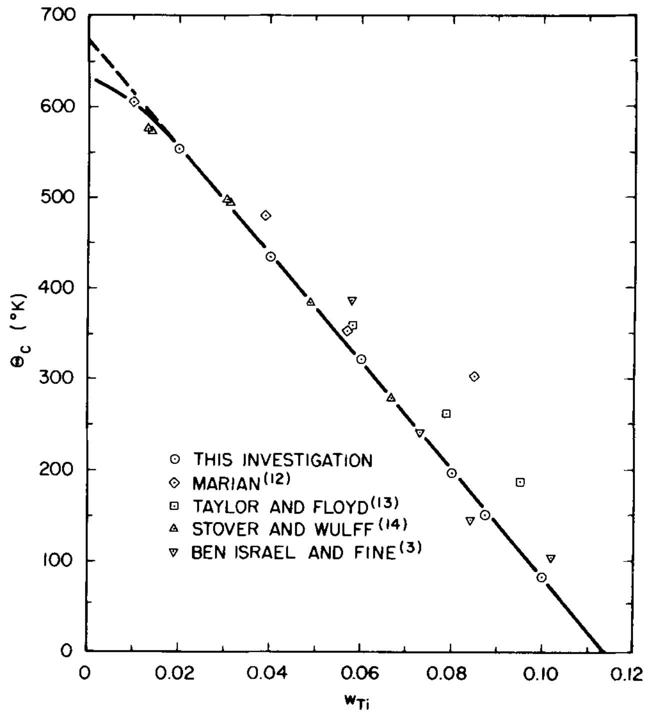


Fig. 1—Calibration curve of the ferromagnetic Curie temperature, θ_c, vs the wt fraction titanium in nickel solid solution.

$$w_{\mathrm{Ti}} = \frac{400 - \theta_c}{5923} \quad [1]$$

with θ_c in °C.

It is interesting to note that θ_c for the 10 wt pct Ti sample is in excellent agreement with the other data. Several investigators[1,3] have noted that precipitation could not be suppressed by quenching in alloys containing the order of 9 to 10 wt pct Ti. However, the result in Fig. 1 suggests that decomposition was completely suppressed by the quenching procedure used in this study.

Aging Studies. The specimens used for the aging studies (8.74 pct Ti) were solution treated for $\frac{1}{2}$ hr at 1000°C, and quenched into the refrigerated brine solution. To prevent oxidation during solution-treatment the thin sheet samples were sandwiched between foils of the Ni-Ti alloy, and the rod samples were placed in a small container made of the same alloy. The samples were packaged in zirconium foil as an additional precaution. The quenching rate was sacrificed somewhat by this procedure, but this sacrifice insured a stable grain size in the aged samples. Surface oxidation of the samples during this treatment was minimal.

The aging times and temperatures in this investigation were chosen to correspond to those in the investigations of Ben Israel and Fine, Dawance *et al.*, and Sass and Cohen. Aging was done in a furnace controlled to within ±1°C at three different temperatures, 692°, 593°, and 525°C, in an atmosphere of flowing titanium-gettered argon. A zirconium foil wrapping was also used to prevent excessive oxidation during aging at the highest aging temperature (692°C). After each aging treatment the specimens were quenched into the refrigerated brine solution. Magnetic analysis was used to follow the aging process at all three temperatures, but the transmission electron microscopy studies involved only the specimens aged at 692°C.

In the magnetic investigation of coarsening of γ' Ni-Al alloys[8] it was found that the shape of the ferromagnetic transition curve and θ_c were strongly affected by the rate at which the specimen was cooled from the aging furnace. Similar effects were anticipated for the Ni-Ti alloys and found in the following series of experiments. The rod specimen aged at 692°C was quenched into the refrigerated brine solution in the normal way after 1 hr. The ferromagnetic transition curve is shown in Fig. 2, and θ_c for this specimen was −93.8°C (w_{Ti} = 0.08337). The same specimen was then reinserted into the furnace (without the zirconium-foil wrapping) for an additional minute and quenched. θ_c for this treatment was −93.0°C (w_{Ti} = 0.08324), which is a change of only 0.15 pct. This is well within the limit of absolute accuracy of the experiments and shows that the effect of the zirconium wrapping was negligible. The specimen was again reinserted into the aging furnace for 1 min (without the zirconium wrapping) and now air-cooled. The ferromagnetic transition curve for this specimen is also shown in Fig. 2. It is significantly broader than the curve for the quenched sample and has a considerably higher θ_c of −85.8°C (w_{Ti} = 0.08202). The experiments above were repeated on samples aged at 525°C, but there was no significant difference between θ_c for air-cooled and quenched samples.

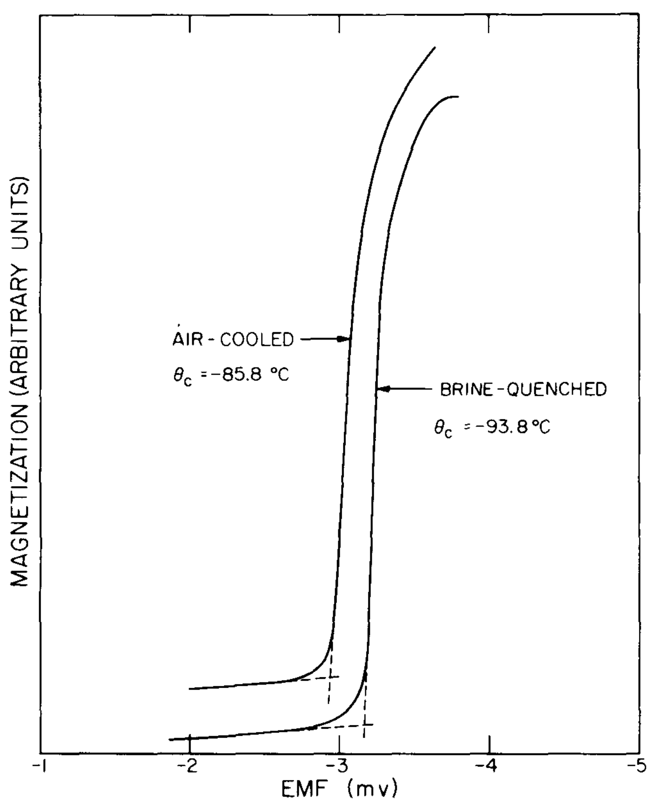


Fig. 2—Tracings of the automatically recorded curves of specimen magnetization vs thermocouple electromotive force for a Ni-8.74 wt pct Ti specimen aged for 1 hr at 692°C. The two curves illustrate the effect of brine-quenching and air-cooling the same specimen from the aging temperature.

Experimental Errors and Uncertainties. For reasons that will become apparent, the absolute values of w_{Ti} reported herein are accurate to within ±1 pct. The absolute accuracy is limited by the uncertainties in the titanium-contents of the alloys used to establish the calibration curve of θ_c vs w_{Ti}, Fig. 1. However, owing to the strong dependence of θ_c on w_{Ti}, Eq. [1], very small changes in w_{Ti} can be readily detected, with an accuracy limited by the determination of θ_c for the aged samples. The uncertainty in the measured values of θ_c is approximately ±0.1°C, and the relative values of w_{Ti} are therefore accurate to approximately ±0.00002.

The γ' particle size measurements are affected by instrumental and contrast limitations. The magnification in the electron microscope was calibrated as a function of the objective lens current, so the magnification values are accurate to within 5 pct. The contrast in dark-field images from superlattice reflections of the γ' precipitates is relatively poor in the case of Ni_3Ti because the difference between the atomic scattering factors of nickel and titanium is fairly small. Therefore, the superlattice reflections are not very intense even under ideal diffracting conditions. Although no particular difficulties were encountered in obtaining aberration-free dark-field images in this investigation, it is impossible to estimate the number of γ' particles that may have been invisible in a given dark-field image. Thus, it is doubtful that the particle sizes reported herein are accurate to better than 10 pct.

RESULTS

If γ' grows by diffusion-controlled coarsening, as hypothesized by the author,[9] the results of this study should then fulfill all the predictions of the Lifshitz-Wagner theory.[10,11] The data that follow are presented in a manner consistent with this adopted point of view.

Magnetic Analysis. The data from the Curie temperature measurements are shown in Fig. 3. Values of w_{Ti} were obtained from the measured values of θ_c according to Eq. [1]. The data in Fig. 3 are plotted as w_{Ti} vs $t^{-1/3}$, which is consistent (apart from the concentration units) with the theoretical equation[9,10]

$$c - c_e = (\kappa t)^{-1/3} \qquad [2]$$

which describes the asymptotic variation of the solute content (c) of the matrix with aging time. In Eq. [2] c_e represents the concentration of solute in the matrix in equilibrium with an infinitely large γ' particle and κ is a rate constant given by

$$\kappa = \frac{D(RT)^2}{9\gamma^2 c_e^2 V_m} \qquad [3]$$

where D is the diffusion coefficient of titanium in nickel, γ is the specific free energy of the γ'-matrix interface, V_m is the molar volume of γ', and RT has its usual meaning.

The values of w_{Ti} approach the predicted linear dependence on $t^{-1/3}$ after aging times that are clearly temperature-dependent: ≃20 min at 692°C; ≃1 hr at 593°C and ≃16 hr at 525°C. It is emphasized that these aging times do not necessarily represent the times at which coarsening actually commences, because Eq. [2] is an approximation[9] which is not accurate at the

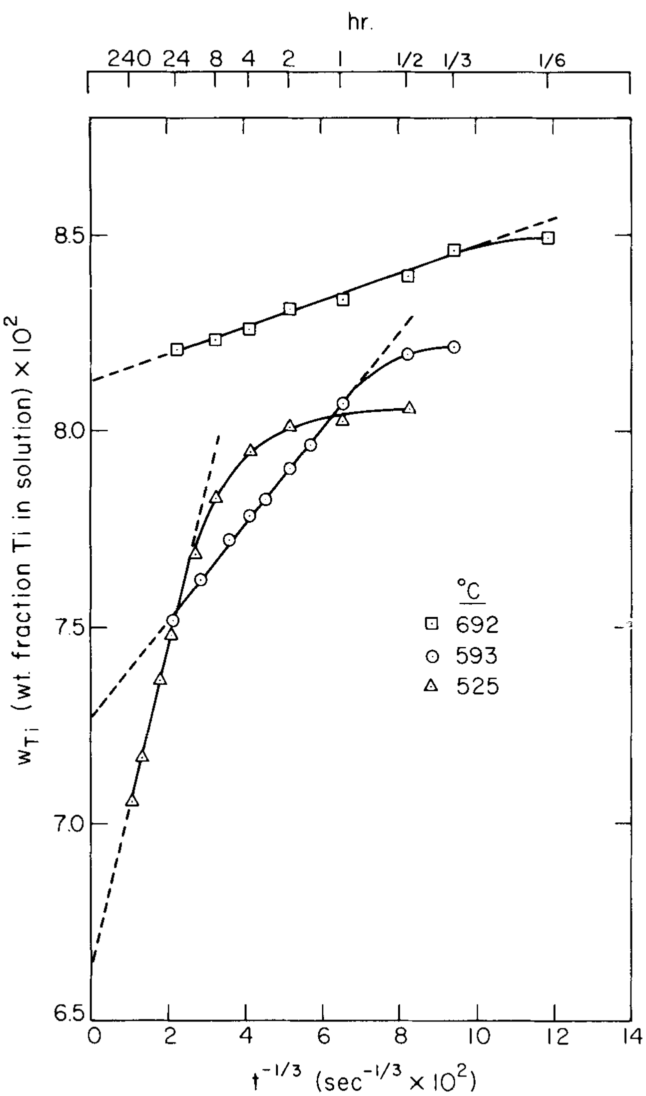


Fig. 3—The variation of the titanium content of nickel-rich matrix during growth of the γ' precipitate, plotted as wt fraction Ti vs $t^{-1/3}$.

beginning of the coarsening process. However, the error involved in using Eq. [2] over the whole range of aging times is generally small, and Eq. [2] is particularly convenient to use for the purpose of evaluating c_e and κ. To this end, the data points in the linear regions in Fig. 3 were least-squares analyzed to obtain values of the intercepts (c_e or w_e) and slopes ($\kappa^{-1/3}$) of the curves. The values of these parameters are summarized in Table I.

According to Eq. [3] the activation energy for the coarsening process can be obtained by plotting $\log(\kappa w_e^2/T^2)$ vs $1/T$. A plot of this type is shown in Fig. 4. The resulting activation energy is 67,500 cal per mole, which is in fair agreement with the re-

Table I. Results of the Least-Squares Analysis of the Data in Fig. 3

T(°C)	$\kappa^{-1/3}$ (sec$^{1/3}$)	$w_e \times 10^2$
525	4.050×10^{-1}	6.633
593	1.235×10^{-1}	7.268
692	3.455×10^{-2}	8.123

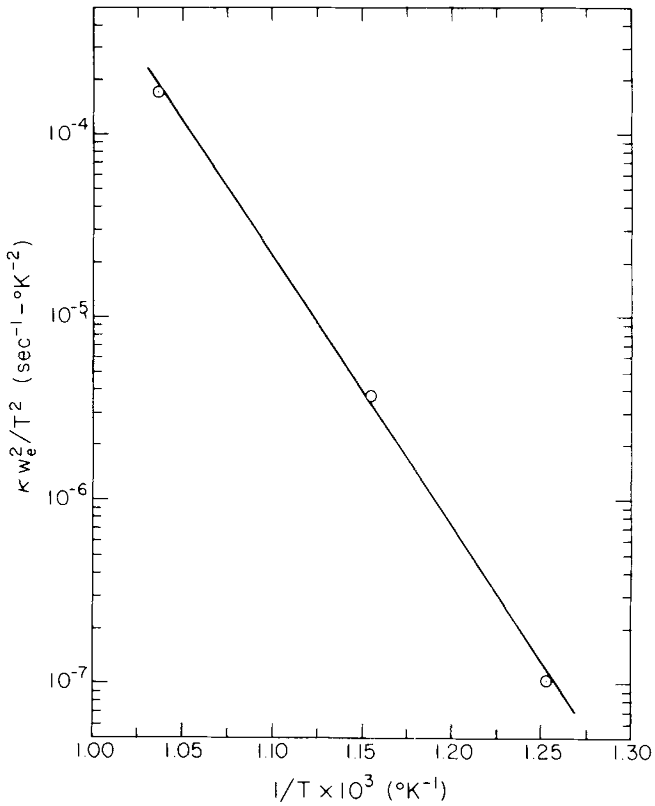


Fig. 4—Plot of the rate constants κ multiplied by the temperature dependent factor w_e^2/T^2 vs the reciprocal of the absolute temperature.

ported value of 61,400 cal per mole for the diffusion of titanium in very dilute Ni-Ti alloys.[16]

Transmission Electron Microscopy Studies. Fig. 5 shows a set of dark-field micrographs of specimens aged for 30 min, 8 hr, and $24\frac{1}{4}$ hr at 692°C. These micrographs illustrate that γ' in Ni-Ti behaves similarly to γ' in Ni-Al in that the γ' particles line up along $\langle 100 \rangle$, and the degree of alignment becomes more pronounced as aging proceeds.[6]

To determine the distribution of particle sizes the edge lengths, a, of 500 cube-shaped γ' precipitates, were measured along the [100] direction, and placed into one of a number of convenient size intervals. The average particle size $\bar{a}$ was evaluated from each histogram, and the histograms were then normalized according to a previously used procedure[7] for comparison with the theoretical distribution of the Lifshitz-Wagner analysis. The normalized experimental histograms, $\frac{9}{4}\bar{a}g(a,t)$, where $g(a,t)$ is the unnormalized histogram, are plotted against the normalized particle size $\rho = a/\bar{a}$ in Fig. 6, where the theoretical distribution, $\rho^2 h(\rho)$,* is also shown for comparison. It is evi-

*
$$h(\rho) = \begin{cases} \left(\dfrac{3}{3+\rho}\right)^{7/3}\left(\dfrac{3/2}{3/2-\rho}\right)^{11/3} \exp\left(\dfrac{-\rho}{3/2-\rho}\right); \rho < 3/2 \\ 0; \rho > 3/2. \end{cases}$$

dent from Fig. 6 that the experimental histograms are considerably broader than the theoretical distribution function, and that they deviate from the theoretical distribution even at low values of ρ (*i.e.*, $\rho < 1$).

Average particle sizes were also obtained from dark-field electron micrographs for three other aging

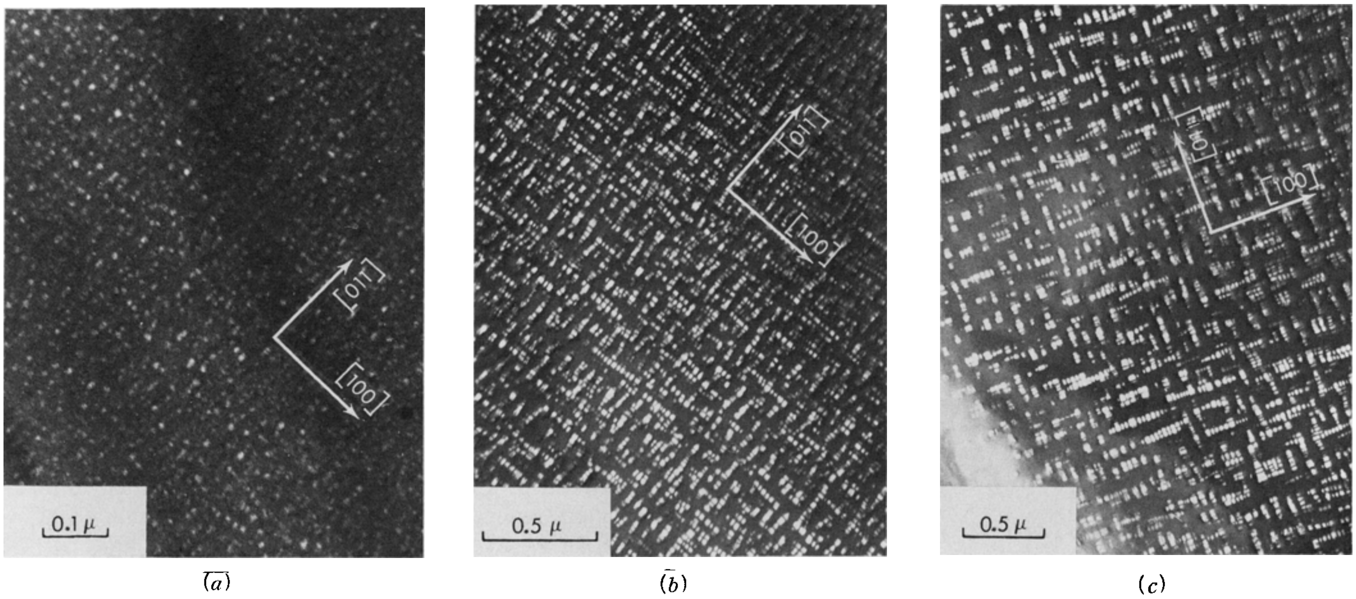


Fig. 5—Electron micrographs of γ' precipitates in a Ni-8.74 wt pct Ti alloy aged at 692°C for: (a) 30 min; (b) 8 hr; (c) $24\frac{1}{4}$ hr. The images are dark-field images from $\{100\}_{\gamma'}$ superlattice reflections. All foils are oriented (011).

times at 692°C (1, 2, and 4 hr). These measurements represented the average of fifty individually measured particles. The data are shown in Fig. 7 as a plot of $\bar{a}/2$ vs $t^{1/3}$, in accord with the theoretical growth equation[10,11] written for cube-shaped particles,

$$(\bar{a}/2)^3 - (\bar{a}_0/2)^3 = kt \qquad [4]$$

where $\bar{a}_0$ is the average edge length at $t = 0$ (the onset of coarsening) and k is a rate constant given by

$$k = \frac{8\gamma c_e D V_m^2}{9RT} \qquad [5]$$

The symbols in Eq. [5] have the same meaning as those in Eq. [3]. The representation in Fig. 7 is accurate provided $\bar{a}_0 \simeq 0$, an assumption which is evidently justified by the fact that coarsening commences as early as 20 to 40 min at 692°C, Fig. 3. No apparent reason could be found for the scatter in the data in Fig. 7.

Evaluation of the Parameters γ and D. The parameters γ and D are readily evaluated from the experimental values of $\kappa^{-1/3}$ and $k^{1/3}$ (the slope of the plot in Fig. 7) according to the equations[9]

$$\gamma = \frac{(k/\kappa)^{1/3} RT}{2 c_e V_m} \qquad [6]$$

and

$$D = \frac{9}{4}\,\frac{(k^2\kappa)^{1/3}}{V_m} \qquad [7]$$

Substitution of the values of the parameters pertinent to 692°C ($k^{1/3} = 3.47 \times 10^{-8}$ cm/sec$^{1/3}$, $\kappa^{-1/3} = 6.42 \times 10^{-3}$ mole sec$^{1/3}$/cm^3, $c_e = 1.51 \times 10^{-2}$ mol/cm^3, $V_m = 27.83$ cm^3/mol) into Eqs. [6] and [7] yields the values of γ and D shown in Table II. The value for the diffusivity of titanium in dilute Ni-Ti alloys, obtained by extrapolating the data of Swalin and Martin[16] to 692°C, is also shown in Table II.

Table II. Estimated Values of γ and D from the Application of Coarsening Theory to the 692°C Data

γ (erg/cm^2)	D (cm^2/sec)	D (cm^2/sec)*
21.3	1.51×10^{-14}	1.08×10^{-14}

*Calculated from the equation $D = 0.86 \exp(-61{,}400/RT)$ given by Swalin and Martin.[16]

DISCUSSION

Almost all the data of this investigation are consistent with the hypothesis that γ' grows by diffusion-controlled coarsening in Ni-Ti alloys after relatively short aging times. The data from the magnetic measurements, Fig. 3, clearly obey Eq. [2] very accurately for $t > 24$ hr at 525°C. We reiterate that the time to reach the linear behavior predicted by Eq. [2] does not necessarily represent the onset of coarsening. However, it is reasonable to assume that coarsening commences within a factor of two of the aging times that linear behavior is observed. We can thus place the onset of γ' coarsening to within 20 to 40 min at 692°C, 1 to 2 hr at 593°C and 24 to 48 hr at 525°C.

In spite of the scatter in the average particle size measurements, the experimental rate constants $k^{1/3}$ and $\kappa^{-1/3}$ yield the very reasonable values for γ and D at 692°C in Table II. The value of γ ($\approx$21 erg/cm^2) is comparable to the value of γ obtained from analysis of coarsening data for γ' in Ni-Al alloys ($\approx$13 erg/cm^2).[8] This is very encouraging because γ should be small,[7] and there is no reason why γ for the γ'-Ni(Ti) interface should be very different from γ for the γ'-Ni(Al) interface. The value of D from the coarsening analysis is in excellent agreement with the diffusivity obtained by extrapolation of Swalin and Martin's data (see Table II). This may be fortuitous for two reasons: a) the value of D from the coarsening analysis is subject to an uncertainty caused by the very broad experimental histograms. If this is corrected for by an empirical procedure suggested by the author,[17] the value of D is approximately a factor of 3 times the Swalin-Martin value; b) there is a crepancy between the value of Q from Fig. 4 and the value of Q determined by Swalin and Martin. Nevertheless, in view of the fact that the titanium concentrations associated with γ' coarsening are very high compared to the concentrations in the dilute Ni-Ti alloys used by Swalin and Martin, the overall agreement between the independent values of D and Q is very good.

It has been shown elsewhere[18] that the values of w_e in Table I unambiguously represent the coherent solubilities of γ' in Ni-Ti alloys. The results of that study are shown in Fig. 8 where the concentration units are in atom fraction titanium. It is evident that the coherent γ' solubilities exceed the solubility of the stable η phase, which they must from thermodynamic considerations. Over the temperature range of this study the equilibrium solubility of γ' obeys the relationship

$$a_e = 0.2566 \exp(-1850/RT) \qquad [8]$$

The electron metallography datum in Fig. 8 represents the result of a dissolution experiment designed to test the significance and accuracy of Eq. [8]. Samples of the 8.74 wt pct (10.50 at. pct) Ti alloy were aged at 700°C for 48 hr to produce coherent γ' precipitates. Individual samples were then reaged for $1\frac{1}{2}$ hr at temperatures near the solubility limit predicted by extrapolating Eq. [8] to 10.50 at. pct Ti (this temperature

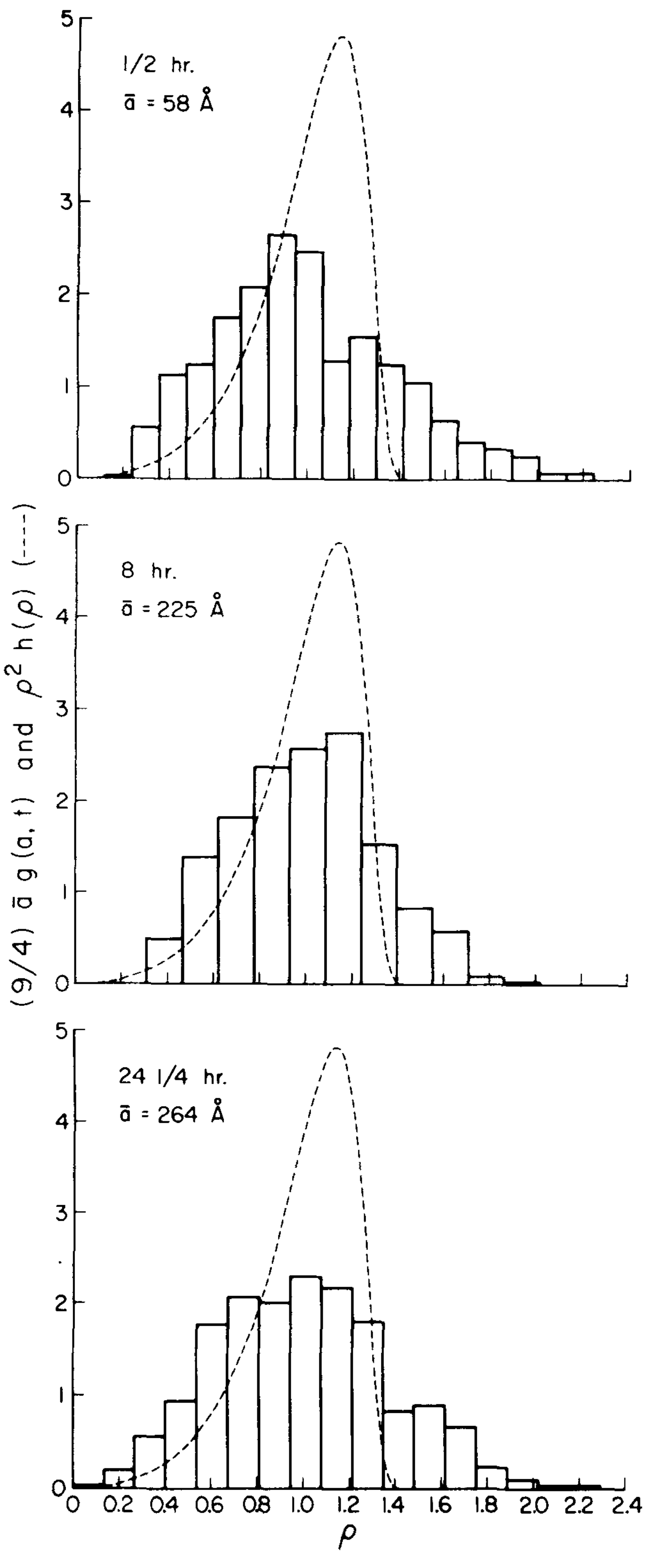


Fig. 6—Histograms showing the γ' particle-size distributions in a Ni-8.74 wt pct Ti alloy aged at 692°C. The histograms are plotted as $\frac{9}{4}\bar{a}g(a,t)$ for comparison with the theoretical distribution function $\rho^2 h(\rho)$, where $\rho = a/\bar{a}$.

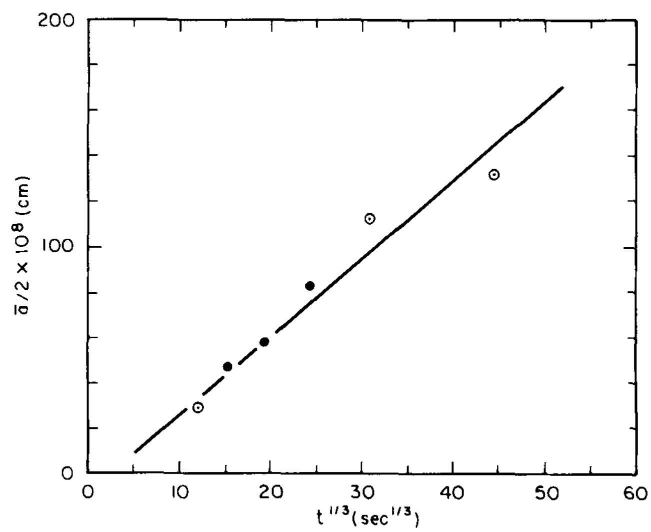


Fig. 7—Plot of half the average γ' particle edge length vs $t^{1/3}$ for a Ni-8.74 wt pct Ti alloy aged at 692°C. The open circles represent data obtained from the histograms in Fig. 6 and the filled circles represent the average of fifty individually measured particles.

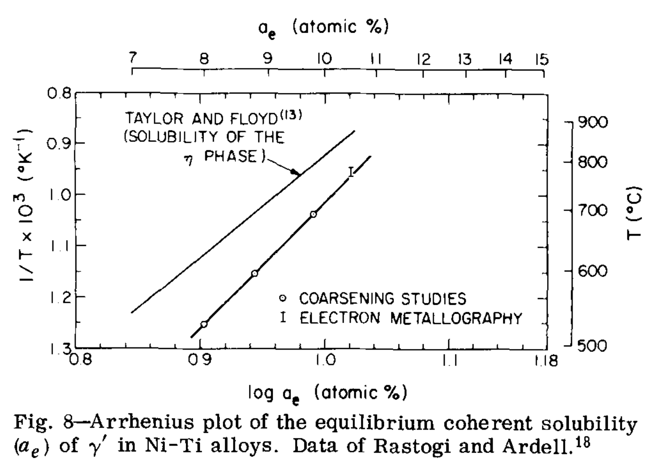
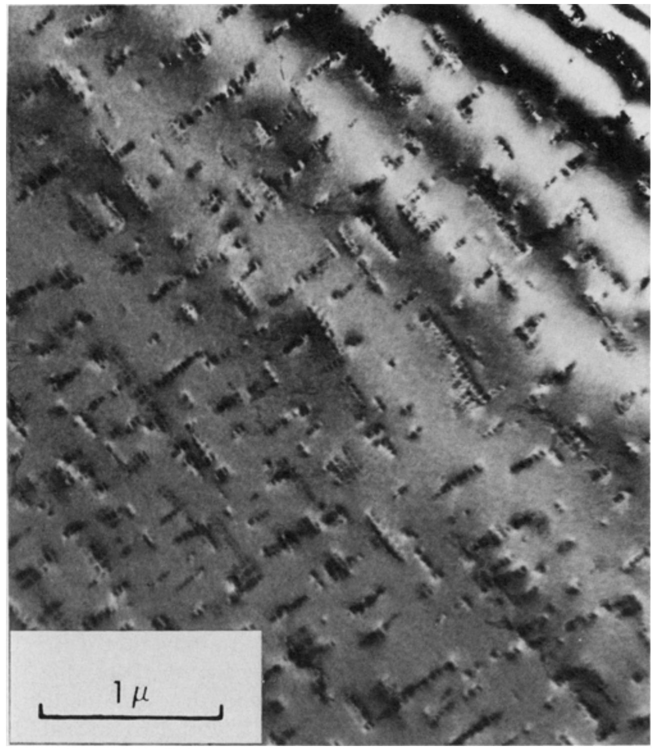


Fig. 8—Arrhenius plot of the equilibrium coherent solubility (a_e) of γ' in Ni-Ti alloys. Data of Rastogi and Ardell.[18]

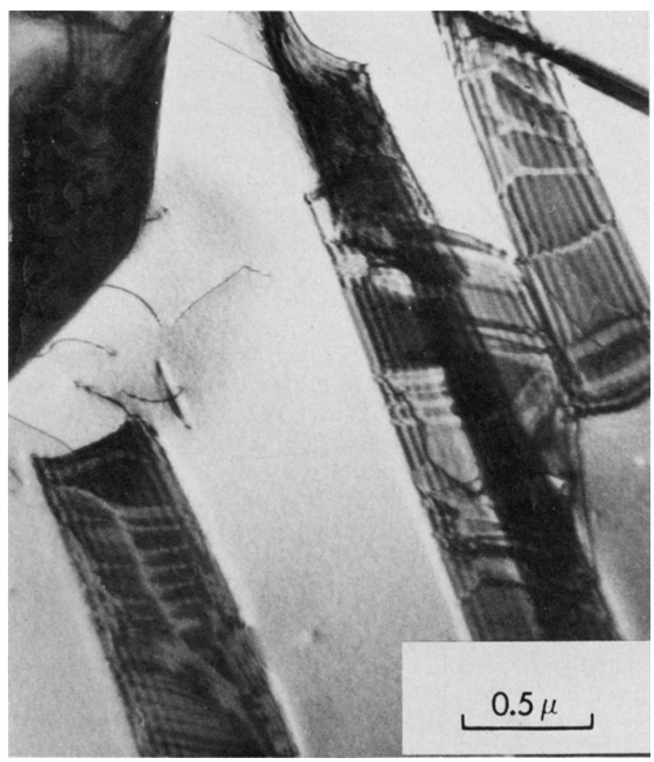
is 768°C). If Eq. [8] describes the coherent γ' solvus, the coherent γ' precipitates that formed on aging at 700°C should dissolve or transform to the more stable η phase on reaging at a temperature just above the coherent solubility limit, whereas coherent γ' should still be present in a sample reaged just below the coherent solubility limit. Typical microstructures resulting from the dissolution experiments are shown in Fig. 9. The observation that the γ' precipitates present in Fig. 9(*a*) have been replaced completely by the η precipitates seen in Fig. 9(*b*) (a difference in reaging temperature of only 9°C), and that these structures bracket the predicted coherent solubility limit of 768°C for this alloy, justifies the conclusion that Eq. [8] describes the coherent solvus for γ' in Ni-Ti alloys over the temperature range 525° to 775°C. Furthermore, the results in Fig. 9 place the accuracy of the data in Fig. 3 (and, by implication the calibration curve, Fig. 1) to within ±1 pct of the absolute titanium content, and provide convincing evidence that the γ' precipitate does indeed grow by diffusion-controlled coarsening after relatively short aging times.

The only important discrepancy between the results of this investigation and the predictions of the Lifshitz-Wagner theory is associated with the distribution of particle sizes. Although the experimental size-distributions fulfill the requirement of being quasi-steady, *i.e.*, independent of aging time within the limits of experimental uncertainty, they are much broader than the theoretical distribution, Fig. 6. The size distributions for γ' in Ni-Ti alloys, are, in fact, much broader than those observed in all other systems where particle coarsening is the established mode of growth. In those other systems (isoamyl alcohol droplets in water,[19] γ' in Ni-Al[7] and Ni-Cr-Al,[20] α-Mn in Mg,[21] θ'' in Al-Cu[22]) the particle size distributions are comparable to each other and are slightly broader than the theoretical distribution. The systems above are very diverse from the structural point of view, making it difficult to isolate any single factor as the cause of the relatively small and nearly constant discrepancy between the experimental and theoretical distributions. However, among the nickel-base alloys containing coherent γ' precipitates, there now appears to be a reasonable correlation between the deviation from the theoretical size distribution and the γ'-matrix lattice mismatch $\Delta a/a = (a_{\gamma'} - a_{\text{matrix}})/a_{\text{matrix}}$. The value of $\Delta a/a$ for γ' in Ni-Ti alloys is +0.9 pct,[23] which is much larger than $\Delta a/a$ for γ' in Ni-Al alloys (+0.6 pct)[24] and γ' in Ni-Cr-Al alloys (+0.1 pct).[20] The problem that needs to be solved is the manner in which the elastic energy associated with $\Delta a/a$ affects the particle size distributions.

There are two ways that strain energy could influence the distribution of particle sizes: a) by affecting the equilibrium γ' particle shape; b) through elastic interactions among the γ' precipitates. In nickel-base alloys containing γ' precipitates we evidently cannot have effect a) without also having effect b). There is a clear trend towards cube-shaped γ' particles as $\Delta a/a$ increases, *i.e.*, in Ni-Cr-Al ($\Delta a/a$ = 0.1 pct) γ' particles are spherical[20] and in Ni-Ti ($\Delta a/a$ = 0.9 pct γ' particles are nearly perfect cubes. Systems with intermediate values of $\Delta a/a$ (*e.g.*, Ni-Al) produce γ' particles intermediate in shape between spheres and cubes (cuboidal). In systems where γ' particles are cuboidal or cubic in shape, pronounced alignment of the particles along ⟨100⟩ is observed, which has been



(*a*)



(*b*)

Fig. 9—Results of the dissolution experiment designed to test Eq. [8]. The Ni-8.74 wt pct Ti (10.50 at. pct Ti) specimen was aged at 700°C for 48 hr and reaged for $1\frac{1}{2}$ hr at: (*a*) 766°C; (*b*) 775°C.

shown to be due to elastic interactions among the γ' precipitates.[6] The existence of elastic interactions among γ' precipitates is a consequence of the difference in shear modulus between γ' and the matrix, as well as a nonzero value of $\Delta a/a$. In the case of γ' in Ni-Al alloys the interaction is attractive because Ni_3Al has a lower shear modulus than the matrix.[6] Therefore, in addition to the usual driving force for coarsening (reduction of the interfacial free-energy of the system), there is a driving force which tends to bring particles closer together, reducing the elastic energy of the system as well.

Although we are as yet unable to account for the effect of strain energy on the distribution in a quantitative manner, it is not unreasonable to assume that the system of particles can grow by diffusion-controlled coarsening with distributions that deviate markedly from the theoretical distribution, provided the distribution is quasisteady and all the other requirements of the Lifshitz-Wagner theory are fulfilled.

Comparison with Other Investigations. The conclusions of this study are evidently in disagreement with those of Ben Israel and Fine,[3] Dawance *et al.*[4] and Sass and Cohen.[5] The disagreement is accentuated by the quantitative comparison of the present magnetic analysis data with Ben Israel and Fine's results. This comparison is shown in Fig. 10, where it is seen that the titanium concentrations of Ben Israel and Fine are significantly lower than those of this study. We can account for part of this discrepancy by recalling the experiments described earlier on the effect of quenching from the aging furnace on θ_c. It was demonstrated, Fig. 2, that air-cooling the specimen aged at 692°C produced an error in θ_c of +8°C, which corresponds to a concentration error of −0.135 wt pct Ti. Similar effects were observed on air-cooled aged Ni-Al alloys, and a consistent and logical mechanism to account for the raising of θ_c has already been proposed.[8] It was suggested that the nickel-rich matrix could undergo additional decomposition on a very fine scale if the aged specimens were not cooled rapidly enough from the aging temperature. This suggestion has been strikingly confirmed by the experiments of Beardmore,[25] who directly observed "hyperfine" γ' precipitates in aged Ni-Al and Ni-Cr-Al alloys that were relatively slowly cooled from the aging temperature. It is reasonable to conclude that hyperfine γ' precipitation also occurs in slowly cooled aged Ni-Ti alloys. This being the case, the measured value of θ_c will not be characteristic of the matrix solid solution that existed at the aging temperature, but will instead reflect the titanium content after the additional depletion that must accompany the formation of hyperfine γ'. The measured value of θ_c will, of course, be higher than if the specimen were water-quenched, and the corresponding value of w_{Ti} will be lower.

Hyperfine γ' precipitation during quenching is undoubtedly responsible for part of the discrepancy observed in Fig. 10, because Ben Israel and Fine not only used specimens with a diameter of about 5.5 to 6 mm (*cf.* ≃1 mm in this study), but *air-cooled* them from the aging temperature (M. E. Fine, private communication). However, hyperfine γ' precipitation would certainly not have affected all of Ben Israel and Fine's measurements because the extent of hyperfine γ' precipitation has been shown to be dependent upon aging temperature[25] (it was also observed that air-cooling the small specimens used in this study from 525°C had no effect on θ_c). Keeping in mind that the relatively large dimensions of the samples used by Ben Israel and Fine, and their relatively slow quenching medium (air) are both factors which promote the formation of hyperfine γ', we can compare the two sets of data in a meaningful way. First, there will probably be little, if any, hyperfine γ' precipitation in samples aged at 525°C, irrespective of sample size and cooling rate, within reasonable limits. In this sense, it is encouraging that the discrepancy between the two sets of data for 525°C aging is small compared with discrepancy observed at the higher aging temperatures. A discrepancy does indeed exist at 525°C, but a consistent explanation eludes the author. The discrepancy increases with increasing aging temperature, and for those samples aged at 700°C, it rises to a full 1 wt pct Ti. This means that if Ben Israel and Fine had water quenched their samples from 700°C instead of air-cooling them, the Curie temperatures would have been lower by about 60°C if hyperfine γ' precipitation was the only source of error. Although we can certainly expect hyperfine γ'

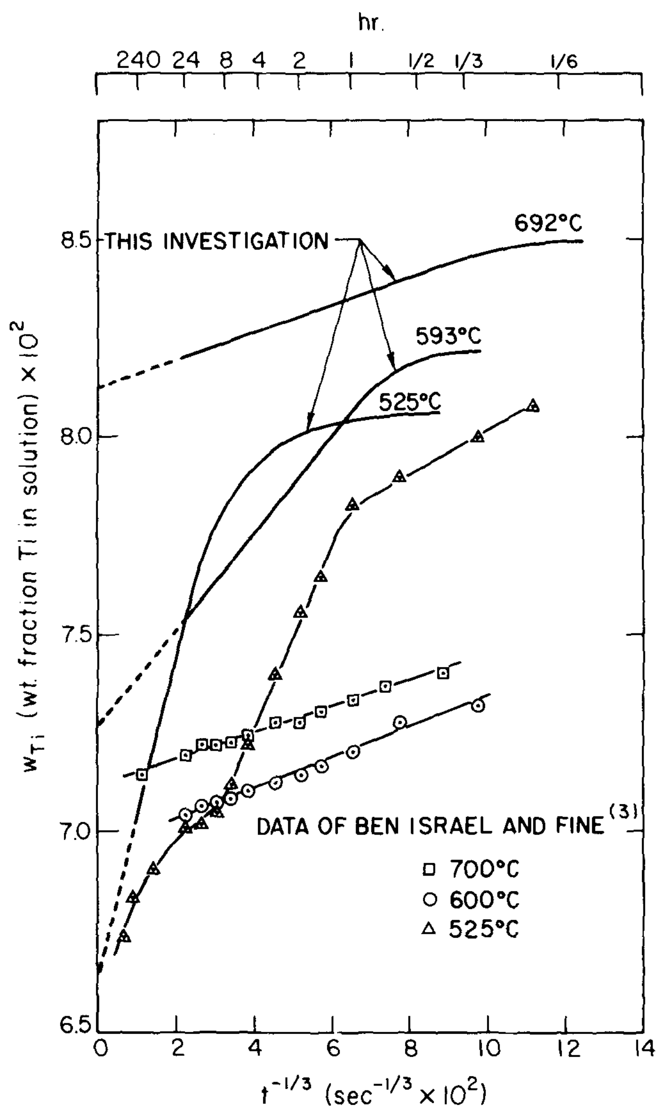


Fig. 10—Comparison of the data of Ben Israel and Fine[3] with the results of this investigation.

precipitation in Ben Israel and Fine's samples (700°C aging) to have produced a raising of θ_c in excess of the increase observed in Fig. 2 (8°C) because of their much larger sample size, an error of 60°C appears very unlikely. Evidently, there is a systematic, unexplained source of experimental uncertainty contributing to the observed discrepancy at all aging temperatures. The contribution of hyperfine γ' precipitation, which is significant at 700°C aging but probably nil at 525°C aging, accounts for the remainder of the discrepancy.

The hyperfine precipitation of γ' during air cooling in samples aged at 700°C is probably also responsible for the discrepancy between the volume fractions of γ' measured by Sass and Cohen using quantitative metallography and those measured by the magnetic mass balance technique of Ben Israel and Fine. This discrepancy was cited by Cohen and Fine[26] as evidence against the hypothesis of γ' coarsening and evidence for the presence of an additional phase in the aged alloys, presumably the metastable preprecipitate Ni_6Ti. However, the volume fraction results of Sass and Cohen are actually in very good agreement with the volume fraction of γ' that can be estimated from data in Fig. 3. Assuming that only γ' is present in the alloy aged at 692°C, the volume fraction of γ' varies from 0.02 to 0.04 during the aging times used. Sass and Cohen estimate the volume fraction of γ' to vary between 0.01 and 0.05 during comparable aging times at 700°C. The very favorable comparison between the present data and those of Sass and Cohen suggests that if an additional phase is present at these aging times its volume fraction is insignificant. The discrepancy between Sass and Cohen's values and those of Ben Israel and Fine is due to the fact that hyperfine γ' influenced not only θ_c, but also the saturation magnetization, σ, of the samples aged at 700°C. Both θ_c and σ must be characteristic of the matrix of the aged samples if the magnetic mass balance technique is to be applied with the necessary precision.[27] These requirements will not be fulfilled if the matrix has been further depleted by the precipitation of hyperfine γ' during cooling from the aging temperature.

One of the important conclusions reached by Ben Israel and Fine was that γ' was preceded by the preprecipitate Ni_6Ti* in the aging sequence. The feeling here is that the role of Ni_6Ti in the aging process is still very much open to question. For example, Dawance *et al.* did some deformation experiments on samples aged at 525°C which were designed to test Ben Israel and Fine's suggestion. Dawance *et al.* claimed that their experiments were successful because they observed that θ_c was drastically reduced by severe deformation (90 pct reduction by cold-swaging) of samples aged for short times (*e.g.*, −68°C after 5 hr), whereas θ_c was not severely affected by deforming samples aged for very long times (−12°C after 500 hr). Dawance *et al.* reasoned that the passage of large numbers of dislocations on severe deformation tended to smooth out the composition fluctuations of average composition Ni_6Ti (thus effectively raising the titanium content of the matrix), but had no large effect on shearing relatively large, discrete γ' precipitates. The reasoning here is undeniably sound. However, Sass and Cohen estimate that the average γ' particle size after 100 hr of aging at 525°C is only about 25Å. After 5 hr of aging, then, the γ' particle size would be the order of only 10 to 15Å. Therefore, it does not appear possible to decide which phase (γ' or Ni_6Ti) is present in the alloy after short aging times on the basis of the results of Dawance *et al.*, because 90 pct deformation of either structure should produce similar results.

*On the basis of the calibration curve determined in this investigation, Fig. 2, the "pre-precipitate" detected by Ben Israel and Fine would have a composition close to $Ni_{27}Ti_4$ or $Ni_{6.75}Ti$.

An additional piece of evidence in apparent support of the Ni_6Ti hypothesis was presented by Sass and Cohen. This was the phenomenon of "veining", observed in thin foils of solution-treated alloys by transmission electron microscopy. However, the author has shown[28] that veining is an electropolishing artifact.

In spite of the objections raised here to Ben Israel and Fine's conjectures on the role of Ni_6Ti, there is sufficient experimental evidence available to indicate that the precipitation of γ' is not as straightforward as a simple nucleation and growth reaction followed by diffusion-controlled coarsening. Ben Israel and Fine's observations of a "plateau" region in the aging kinetics, *i.e.*, a time interval during which the quantity used to follow the aging reaction (these include θ_c measurements, hardness and yield stress measurements) does not change appreciably, suggest a two-stage reaction. Saito and Watanabe[29] have also observed plateaus in curves of hardness vs aging time in a Ni-12 at. pct Ti aged at various temperatures. Indeed, even the aging curves herein, Fig. 3, show plateaus at short aging times, where the change of w_{Ti} (or θ_c) is very small compared to the variation during the coarsening reaction. Thus the existence of a two-stage reaction leading to the formation of γ' is apparently well established. That the initial reaction product is Ni_6Ti, as suggested by the low magnetic field studies of Ben Israel and Fine, is perhaps an attractive proposal, but one that remains to be substantiated by unambiguous independent experimentation.

CONCLUSIONS

The results of this investigation are entirely consistent with the hypothesis that the metastable γ' precipitate grows by diffusion-controlled coarsening after relatively short aging times in aged Ni-Ti alloys. The measurements of θ_c as a function of aging time confirm the existence of aging plateaus, first observed by Ben Israel and Fine, but also indicate that γ' coarsening begins shortly after the plateaus are reached. The approximate aging times for the onset of the coarsening reactions are: 20 to 40 min at 692°C; 1 to 2 hr at 593°C; 24 to 48 hr at 525°C. The conclusions of this study are therefore in disagreement with those of Ben Israel and Fine, Dawance *et al.*, and Sass and Cohen, who have postulated that the preprecipitate Ni_6Ti transforms to γ' shortly after the aging plateaus are reached.

The experimental particle-size distributions are significantly broader than the theoretical distribution of the Lifshitz-Wagner theory. They are also broader than the γ' particle size distributions determined in aged Ni-Al and Ni-Cr-Al alloys. It is suggested that this discrepancy is due to the relatively large lattice parameter misfit in the Ni-Ti system (+0.9 pct) as opposed to the smaller misfits in the Ni-Al (+0.6 pct) and Ni-Cr-Al (+0.1 pct) systems. It is emphasized that broad particle size distributions are not inconsistent with the Lifshitz-Wagner theory provided they are quasisteady, *i.e.*, independent of aging time. The distributions observed herein fulfill this condition within the limits of experimental uncertainty.

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