Phase Separation in an Ni–12.5 at.% Al Alloy at 575 K

By J. E. Epperson

Materials Science Division, Argonne National Laboratory, Argonne, IL 60439, USA

J. S. Lin

Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

And P. D. Labarbe

Laboratoire de Science des Matériaux Vitreux, 34060 Montpellier, France

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Abstract

The phase separation in a supersaturated Ni–12.5 at.% Al alloy has been investigated by high-angle diffuse scattering, small-angle scattering, transmission electron microscopy and electrical resistivity methods. High-angle X-ray diffuse scattering measured at room temperature on a bulk single crystal homogenized and quenched from 1323 K showed well developed short-range atomic ordering. An electrical resistivity isochrone shows a marked peak at about 675 K. Small-angle scattering measurements on samples annealed at 823 K clearly indicate that, at this temperature, phase separation occurs by a nucleation and growth process. It has been argued that a cluster coagulation model well represents the processes occurring at 823 K. It is, however, not required that the same process be operational at lower temperatures, particularly below the break in the resistivity isochrone. Measurements for annealing times up to 840 h at 575 K reveal weak small-angle scattering which has some of the characteristics of a continuous transformation. However, much longer transformation times at the lower temperature will need to be investigated before the possibility that this is only a kinetic effect associated with slow nucleation of the second phase can be ruled out.

Introduction

The α-phase Ni–Al alloys are prototypical of an important class of commercial Ni-base alloys whose desirable mechanical properties are attributed to a dispersion of Ni₃Al-type second-phase particles. These precipitates tend to be stable to moderately high temperatures and act as obstacles to dislocation motion, thereby imparting desirable mechanical properties. Understanding the mechanism by which the phase separation occurs would be advantageous in tailoring alloy properties for a given application.

According to classical theories of alloy decomposition (Cahn, 1968), the mechanism of phase separation in a given alloy depends on the temperature at which the separation occurs. More recent theories (Binder, 1977; Gunton, 1984) suggest, however, that the demarcation between the nucleation and growth regime and that in which spinodal decomposition occurs, if the demarcation exists, may not be sharp. In an earlier work (Epperson, Loomis, Faber, Lin & Hendricks, 1987), it was argued convincingly that at 823 K this Ni–12.5 at.% Al alloy decomposes by a nucleation and growth mechanism. The principal goal of this work was to investigate experimentally the decomposition of an Ni–12.5 at.% Al alloy at lower temperatures. An electrical resistivity isochrone was used to survey the decomposition behavior in the range from about 525 to 925 K. Small-angle X-ray scattering measurements were then used to study the phase separation at 575 K, for times up to 840 h. The present contribution is a first incomplete evaluation of these data.

Background

In some careful transmission electron microscopy work on quenched α-phase Ni–Al alloys, Ardell, Nicholson & Eshelby (1966), Ardell & Nicholson (1966) and Phillips (1966) concluded that a modulated microstructure evolved from an initially random spatial arrangement of γ' particles. Elastic interactions were proposed as the driving force for alignment of the particles during coarsening. Beddoe, Haasen & Kostorz (1984) concluded, from a small-angle neutron scattering (SANS) investigation on relatively thick specimens, that even for short aging times at 823, 848 and 898 K the precipitates were preferentially aligned along [100] directions in the matrix. Ardell, Nicholson & Eshelby claimed that at 898 K and above α-phase Ni–Al alloys decomposed by nucleation and growth, and excellent agreement of the observed
growth kinetics with the theoretical predictions for Ostwald ripening by Lifshitz & Slyozov (1961) and by Wagner (1961) was reported. Phillips stated that the precipitation was a single stage process, whereas Williams (1959) proposed that a two-stage process was operating; the first stage was thought to be a period of increasing short-range atomic ordering, and the second stage was believed to be nucleation and growth of coherent platelets of Ni$_3$Al on {100} matrix planes. Cahn (1963; 1966, cited by Phillips, 1966) suggested that the modulated microstructure observed in the early stages of decomposition of some Ni-base alloys could be due to spinodal decomposition. Ben Israel & Fine (1963) proposed that the modulated γ' microstructure observed in some analogous Ni–Ti alloys formed by spinodal decomposition and, hence, that the microstructure was modulated from the beginning. A quotation from Ardell, Nicholson & Eshelby (1966) was disturbing, however. They stated ‘Nucleation has ceased to occur long before our observations have been made’. This statement, in concert with the observations by Manenc (1956, 1959) and by Bagariatski & Tiapkin (1957) that side bands were sometimes observed from samples directly after quenching from the homogenization temperature, raises the important question as to whether these investigations have, in fact, studied the early stages of phase separation in these prototypical Ni–Al alloys.

In a bulk (3 mm thick) Ni–12.7 at.% Al single crystal quenched from 1323 K, Epperson & Fürnrohr (1983) found a well developed short-range-ordered structure, with some evidence for a modulated component of the microstructure. Recently, Epperson, Loomis, Faber, Lin & Hendricks (1987) studied the phase separation at 823 K in thin samples of an Ni–12.7 at.% Al alloy, following rapid quenching from 1333 K. As indicated by small-angle X-ray scattering (SAXS) measurements, transformation in the thin samples was suppressed by the quench; however, both SAXS and electrical resistivity measurements showed that a marked change took place within 15 s of annealing at 823 K. After this period of rapid change, there was an incubation period of about ten hours in which there was minimal net growth of the particle size, and for considerably longer annealing times a coarsening reaction ensued. It was argued that the large and rapid change, in both electrical resistivity and small-angle scattering upon annealing at 823 K, was due to the formation of tiny regions of short-range-ordered Ni$_3$Al. It was further proposed that these tiny ordered regions were the clusters whose existence was assumed in the cluster dynamics model of Binder (1977), that the observed incubation period corresponded to his cluster coagulation regime and that in the coarsening region a classical evaporation-condensation process (Ostwald ripening) occurred. It would not be inappropriate to think of the cluster coagulation process as representing nucleation and growth of the second-phase precipitate particles.

Having established that nucleation and growth are occurring at 823 K we cannot insure that the same decomposition mechanism is operational at still lower temperatures. The goal of the present research was to survey the decomposition behavior over a wide range of temperature with electrical resistivity measurements and to use small-angle scattering to study the transformation at a significantly lower temperature (575 K) than in the previous study.

**Experimental procedure**

Buttons of Ni–12.5 at.% Al were prepared and homogenized, starting with 99.99% Al and 99.998% Ni. These homogenized buttons were then rolled, with intermediate anneals, to 0.2 mm thickness. For the SAXS measurements, disks 3 mm in diameter were stamped from the polycrystalline strip. These disks were annealed for one hour, as a single batch, at 1323 K in flowing H$_2$ and rapidly quenched into iced brine. The transformation anneals were carried out in a KNO$_3$–NaNO$_3$ salt bath, maintained at 575 K, then quenched to room temperature in water. Following mechanical polishing to about 0.1 mm, samples were prepared for SAXS measurements by electropolishing from both sides in an electrolyte consisting of a 1:1 volume mixture of orthophosphoric acid and water, using an applied potential of 22.5 V. The SAXS measurements were carried out at ORNL using the 10 meter X-ray scattering instrument (Hendricks, 1978). This instrument is of the pinhole type and utilizes a two-dimensional position-sensitive gas-filled proportional counter of the Kopp–Borkowski type (Borkowski & Kopp, 1978). In this investigation, Cu Kα radiation monochromated by diffraction from pyrolytic graphite was used.

For the electrical resistivity measurements, samples approximately 0.5 x 7 cm were cut from the 0.2 mm thick sheet stock. Platinum wire current and voltage leads were spot welded onto the samples with the voltage contacts about 5.3 cm apart. The heat-treatment procedure for the resistivity samples was the same as that described above for the SAXS specimens; no further surface preparation was required, however. In order to minimize contributions from phonon scattering, all electrical resistivity measurements were carried out with the sample and its holder maintained at liquid-nitrogen temperature in the apparatus described by Ockers & Berger (1980). The resistivity results are presented as changes relative to the quenched state.

**Results and discussion**

In the following discussion relating to the microstructural features, we shall adopt the glossary of
terms from Epperson, Loomis, Faber, Lin & Hendricks (1987). Electrical resistivity measurements are sensitive to microstructural changes; however, they are not particularly discriminating. Hence, in the present work, the resistivity data will be utilized only to indicate in what temperature regime and on what time scale significant changes are occurring in the supersaturated alloy.

As a means of surveying the decomposition behavior over a relatively wide range of temperature, a 15 s electrical resistivity isochrone for an Ni–12.5 at.% Al alloy has been determined, and the results are shown in Fig. 1(a). The data are shown as percentage changes relative to that of the sample quenched from the homogenization temperature of 1323 K. Aside from the magnitude of the observed resistivity changes, the most striking feature of this figure is the peak at about 675 K. The two most obvious possibilities are: (1) the peak indicates a change in the mechanism of phase separation above and below 675 K for this Ni–12.5% Al alloy, or (2) the peak is an artifact of the kinetics of phase separation.

Electrical resistivity isotherms have been measured at 578 K and at 818 K, and the results are shown in Fig. 1(b); the 578 K isotherm extends from 15 s to 232 h, and the 818 K isotherm is for 15 s to 916.6 h. The initial 15 s anneal at these two temperatures results in similar changes in the resistivity; however, subsequent annealing produces divergent behavior, as shown in Fig. 1(b). Based upon previous high-angle diffuse scattering (Epperson & Fünrohr, 1983) and small-angle scattering results (Epperson, Loomis, Faber, Lin & Hendricks, 1987), it is concluded that the initial abrupt increase in resistivity is due to formation of small ordered regions of Ni₃Al, i.e. short-range atomic ordering. Further annealing at 823 K was found (Epperson, Loomis, Faber, Lin & Hendricks, 1987) to result in phase separation by a nucleation and growth mechanism, well described qualitatively by the cluster dynamics model of Binder (1977). Note that subsequent precipitation at 818 K resulted in a monotonic decrease in the resistivity. In contrast to the 818 K behavior, for times beyond 15 s isothermal annealing at 578 K resulted in a monotonic increase in electrical resistivity, although the rate of increase was slowing toward the end of the time range investigated.

In order to provide additional microstructural information, the small-angle scattering has been measured for selected isothermal annealing times ranging up to 840 h at 575 K, and a typical scattering profile for 114 h annealing is shown in Fig. 2. Motivated by the appearance of the scattering profiles and the considerations discussed above, we examined the small-angle scattering data for possible evidence of spinodal decomposition. Fig. 3(a) shows the amplification factor, \( R(q) \), vs the reciprocal-space variable \( q \); \( R(q) \) is defined by Rundman & Hilliard (1967) as

\[
R(q) = \frac{-(\tilde{D}/f'')(f'' + 2\eta^2 Y + 2K_q q^2)}{q^2},
\]

where \( \tilde{D} \) is the interdiffusion coefficient, \( f''\) is the second derivative of the Helmholtz free energy, \( \eta^2 Y \) is a strain-energy term and \( K_q \) is the gradient-energy coefficient. Qualitatively, the amplification factor shown in Fig. 3(a) has the form expected from Cahn’s linear theory of spinodal decomposition (Cahn, 1961). However, a plot of \( R(q)/q^2 \) vs \( q^2 \), shown in Fig. 3(b), shows marked deviations from the predicted linearity. For the present alloy system, two obvious possibilities for such a discrepancy are: (1) short-range atomic ordering known to be present but not considered in the theory and (2) approximations inherent in the linear theory of spinodal decomposition. A more-comprehensive theory of spinodal decomposition is, in fact, available from Langer, Bar-on & Miller (1975). A comparison of this latter theory with the present data has not been made as yet.

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**Fig. 1.** (a) Electrical resistivity isochrone for 15 s annealing of an Ni–12.5 at.% Al alloy in the range from 525 to 925 K. (b) Electrical resistivity isotherms for Ni–12.5 at.% Al at 818 K and 578 K after homogenization at and quenching from 1323 K.
Because of the presence of the interference peak in the small-angle scattering profile, the Guinier approximation is not strictly valid for this alloy system. Nevertheless, it is commonly used as a means of obtaining a crude estimate of the 'particle' size. This analysis has been carried out for the region in momentum-transfer space beyond the interference maximum, and the resulting mean Guinier radii for this Ni–12.5 at.% Al alloy are shown in Fig. 4 for times up to 840 h at 575 K; the straight line is only a guide to the eye. Even after 840 h at this temperature, the mean particle size is below 8 Å. It has been estimated (Epperson & Lin, 1987) that for this alloy composition at 823 K, the critical radius is about 22 Å. The present experiment does not permit a direct determination of this critical size parameter; however, Wunderlich (1976) has given an expression for the critical radius at temperature $T$ as

$$r^* = 2\gamma T_m/\Delta H p \Delta T,$$

where $\gamma$ is the interfacial energy, $T_m$ the absolute melting temperature, $\Delta H$ the enthalpy of melting, $p$ the bulk density and $\Delta T = T - T_m$. The expression yields an estimate of 13 Å for the critical radius at 575 K, a value consistent with the discussion of Darken & Gurry (1953).

In summary, while the present small-angle scattering results show some of the characteristics of a continuous transformation, one cannot rule out the possibility that the scattering is due to a non-random distribution of very small particles. If the microstructure consists of small particles, the mean Guinier radius does not exceed 8 Å for up to 840 h at 575 K. Small-angle scattering data extending to much longer annealing times will be required to enable one to determine the mode of phase separation in this $\alpha$-phase Ni–Al alloy at 575 K. Experimentally, the electric resistivity measurements would appear to be
the most convenient means to establish this time range. It would be interesting to test the ability of dynamic scaling theories (Lebowitz, Marro & Kalos, 1982; Furukawa, 1983) to project the time required for the particles to reach the critical size.

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References
