Decomposition kinetics in Ni-Ti alloys

A. Cerri,[*] B. Schönfeld, and G. Kostorz

Institut für Angewandte Physik, Eidgenössische Technische Hochschule Zürich, CH-8093 Zürich, Switzerland

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The decomposition of quenched Ni-Ti single crystals has been studied *in situ* by small-angle neutron scattering at 773, 813, and 853 K. Anisotropic scattering patterns were observed from the beginning and attributed to a preferred alignment of the decomposition products along ⟨100⟩. At 853 K the integrated intensity indicates that the composition of the precipitates remains constant after about 200 min. The Ti concentration estimated in this regime (16 ± 3 at.%) is smaller than expected for a coherent, metastable γ' precipitate (Ni_3Ti), possibly because of coherency strains.

The decomposition of a supersaturated alloy (solid solution) obtained by quenching from a homogeneous high-temperature equilibrium state is a good example for the study of dynamical properties of condensed systems far from thermodynamic equilibrium. Metastable and stable states may be reached, involving diffusion of the alloy components and formation of regions of different chemical composition. The early stages of decomposition are controlled by a nucleation-and-growth or a spinodal mechanism (see, e.g., Refs. 1–3) while during the later stages the volume fraction f_v of the precipitate phase remains constant. A further decrease of the free energy of the system is accomplished by particle coarsening[4,5] which reduces the interfacial energy term. At least during this stage, a time-independent scaled scattering function is expected.[2,3] The average size of the precipitates and their average distance are predicted to follow a power law or a logarithmic law, depending on the detailed model (e.g., Ref. 6). Scattering functions and further details of alloy decomposition can be determined experimentally by small-angle scattering of x rays and neutrons.[7–9] Neutrons are particularly useful for heavier elements where x-ray absorption is large, and the present paper reports on in-beam and small-angle neutron-scattering (SANS) studies of decomposition processes in nickel-rich Ni-Ti alloys. The large difference in the neutron-scattering length of the two components allows for very sensitive and precise SANS measurements to be taken.

If a homogeneous, supersaturated Ni-Ti alloy is aged at intermediate temperatures, a metastable ordered phase with $L1_2$ structure (γ' phase) precipitates first, remaining coherent with the matrix. It is well known that during the late stages of γ' precipitation coherency strains influence the morphology and the spatial correlation of precipitates. Using transmission electron microscopy (TEM) Ardell[10] showed that precipitates exceeding a size of ∼6 nm are cuboidally shaped and aligned along ⟨100⟩ directions, but from these investigations it is not clear at which stage the alignment begins. On further aging the coherent γ' phase finally transforms to an incoherent hexagonal phase (η phase, DO_{24} structure), with a Ti concentration of 25 at.%.[11]

Single crystals of Ni-(10.5–11.5) at.% Ti were grown and disks about 2.5 mm thick and 10 mm in diameter

were prepared with a surface normal parallel to a ⟨110⟩ direction. After solution treatment of 1 h at 1373 K in a purified-Ar atmosphere the samples were quenched in water. After a preliminary study of the quenched samples[12] those displaying the "best" homogeneity were selected and mounted in a vacuum furnace specially designed to fit the D11 SANS instrument at the Institut Laue-Langevin (ILL), Grenoble, France. The decomposition reaction was studied *in situ* for about 20 h at 773 and 813 K and for 10 h at 853 K. This allowed early and later stages of decomposition to be followed. (Neutron wavelengths were 0.6 and 0.66 nm, and the sample-detector distance was 1.7 m.) The measuring temperatures were reached within 10 min starting from room temperature and were kept constant during the aging period.

The scattering patterns collected with the two-dimensional position-sensitive detector (64×64 cm^2, 1-cm^2 pixel size) during appropriate time intervals always showed a strong dependence of the SANS intensity on the direction of the scattering vector Q (see Fig. 1 for a typi-
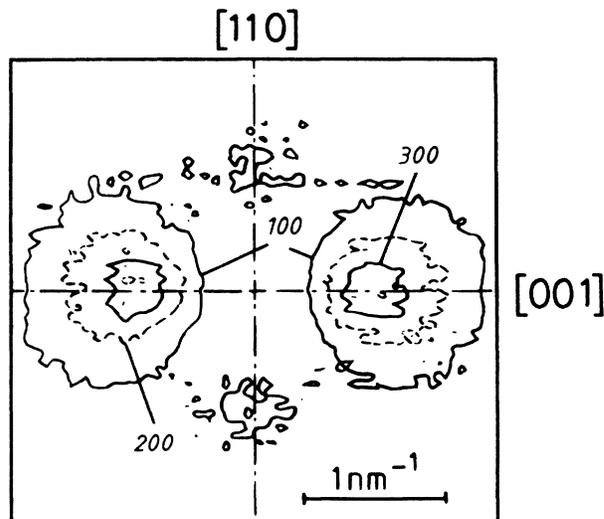

FIG. 1. Scattering pattern of a Ni-11.5 at.% Ti single crystal aged at 813 K for 16 h. Lines of equal counts in ∼17 min are indicated.

cal isointensity plot). Measured intensities were corrected for background and converted to macroscopic differential cross sections using the incoherent scattering of a vanadium single crystal. Cross sections as a function of Q (with $Q = 4\pi\sin\theta/\lambda$ for the modulus of Q, θ is half the scattering angle, λ is the wavelength) along $\langle 100 \rangle$ and $\langle 110 \rangle$ were obtained by averaging the measured intensities for given Q intervals over sectors including cells within $\pm 15°$ around these directions. Figure 2 shows cross sections $I(Q)$ along $\langle 100 \rangle$ and $\langle 110 \rangle$ for the crystals aged at 853 K. The maxima for $Q \neq 0$ indicate that the decomposition products are not randomly distributed in the sample. Spatial correlations are present and particularly pronounced along $\langle 100 \rangle$. Such correlations are well known for the late stages of decomposition in systems with large lattice mismatch between matrix and particle and/or anisotropic elastic prop-
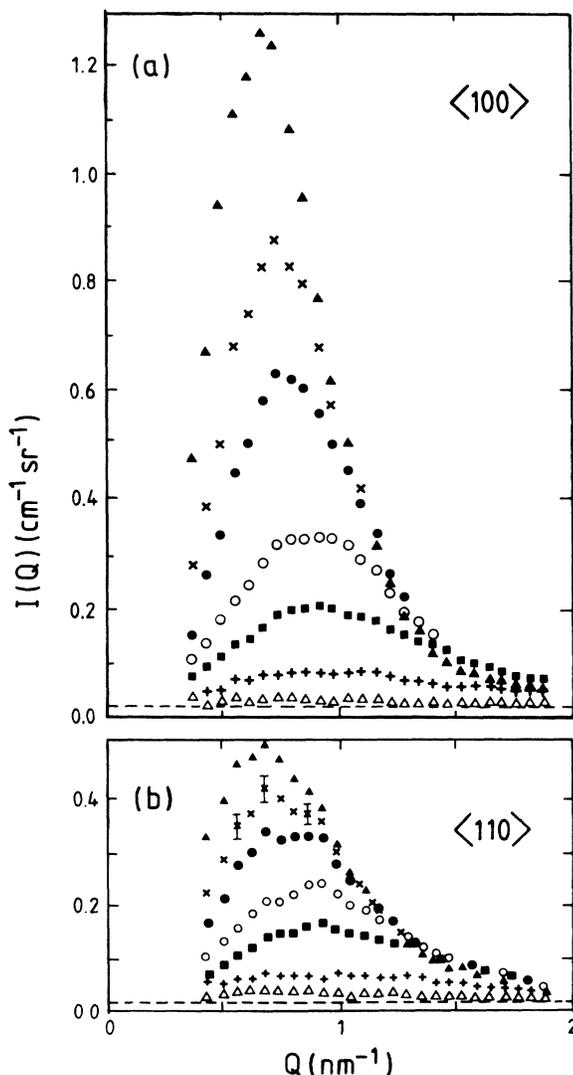
erties. In this stage the particles of the new phase are usually large enough to be observed by conventional TEM. It is often assumed that the particles of the phase nucleate randomly and that the alignment takes place during the coarsening stage. The mechanism of the alignment is currently subject to discussion (see, e.g., Ref. 13). The present results indicate that correlations are present from the earliest stages of decomposition.

With increasing aging time the peak intensities increased, and peak positions $Q_M(t)$ shifted towards smaller scattering vectors. A useful quantity in characterizing the transformation is the integrated intensity

$$\tilde{Q} = \int I(Q) dQ,$$

where the integration includes the whole reciprocal space. Within the two-phase model (see, e.g., Ref. 8),

$$\tilde{Q} = (2\pi)^3 f_c (1 - f_c)(\Delta\rho)^2,$$

where $\Delta\rho$ is the difference between the scattering length densities of the particles and of the matrix. The quantity $\tilde{Q}$ was determined from orientationally averaged data, $I_a(Q)$. At 853 and 813 K (for all but the earliest stages) the accessible Q range extended well into the Porod regime where the intensity decreases as expected according to $I_a(Q) = AQ^{-4} + B$ with $A, B = $const. The constant A determined from such a Porod analysis was used to extend $I = I_a - B$ to larger Q. The contribution of this extrapolated part to $\tilde{Q}$ was about 20% for the longest aging time at 853 K (see Fig. 3 and Ref. 14 for further details). While $\tilde{Q}$ continues to increase beyond $t = 1000$ min for the lower temperatures, $\tilde{Q}$ at 853 K becomes time independent after about 200 min. A constant $\tilde{Q}$ indicates that the precipitation process is completed (f_c is constant). (Ardell[10] found that coarsening sets in at comparable aging times, i.e., within one to two hours at 866 K, for an alloy containing 10.5 at.% Ti.) This also implies that the Ni-Ti matrix has reached its (metastable) terminal Ti concentration, c_m, which is ~ 8.6 at.% at this temperature.[15] The Ti concentration of the precipitates c_p can thus be estimated from the experimental value of $\tilde{Q}$ as $\Delta\rho$ and f_c depend only on c_m and c_p. A value of 16 ± 3 at.% Ti was obtained for c_p. This value deviates considerably from the value of 25 at.% Ti expected for the ordered γ' phase. That a concentration of 25 at.% Ti may (at least for a transitional period)
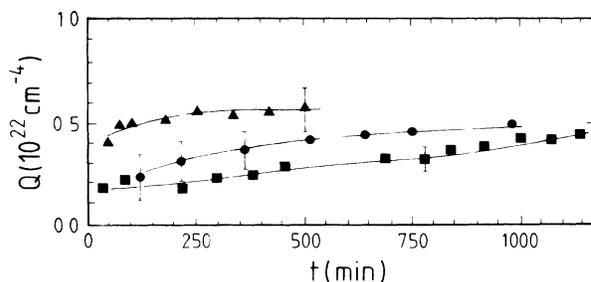

FIG. 2. Coherent SANS intensity from a Ni–11.5 at.% Ti single crystal aged in situ at 853 K for different aging times. (a) Q along $\langle 100 \rangle$, (b) Q along $\langle 110 \rangle$. △: As quenched; +: Aged for 2.1 min; ■: 46 min; ○: 101 min; ●: 220 min; ×: 320 min; ▲: 506 min. Broken lines indicate the Laue scattering of a random Ni–11.5 at.% Ti solid solution.

FIG. 3. Integrated SANS intensity as a function of aging time. ■: Ni–11.5 at.% Ti, aging at 773 K; ●: 10.5 at.% Ti, 813 K; ▲: 11.5 at.% Ti, 853 K. Lines are to guide the eye.

not be reached, has also been reported by Grüne[16] whose interpretation of field-ion atom-probe experiments on Ni-12 at.% Ti aged at 823 K, however, admits the presence of Ni_3Ti. Yoshida et al.,[17] using high-resolution electron microscopy, have found small circular ordered regions in slightly decomposed Ni-Ti alloys and suggest the possibility of an ordered transitional phase $Ni_3(Ti_x-Ni_{1-x})$. For a simple model system recent calculations[18] show that coherency strains may considerably influence volume fraction and chemical composition of (metastable) equilibrium phases compared with those of the unstressed system. The present results may be taken as an indication that in the Ni-Ti system coherency strains affect the spatial distribution as well as the composition of the precipitate phase.

Dividing the orientationally averaged scattering curves $I(Q)$ by the integrated intensity, one obtains a reduced structure function $S(Q)$. In the coarsening stage, $S(Q,t)$ should vary according to

$$S(Q,t) = L^{-3}(t)F(x) ,$$

where $L(t)$ is the time-dependent characteristic length scale of the system (corresponding to the average linear dimension of the precipitate phase), $x = QL(t)$, and $F(x)$ the appropriate scaling function. $L(t)$ can be obtained from the reciprocal value of $Q_M(t)$, or one can use the radius of gyration, $R_G(t)$,[7] or $M_1^{-1}(t)$, the reciprocal value of the first moment of $S(Q,t)$, $M_1(t) = \int S(Q,t)Q\,dQ/\int S(Q,t)dQ$. The radius of gyration R_G follows from $S(Q,t) \propto \exp(-Q^2R_G^2/3)$ which is valid for a dilute system of identical, randomly oriented particles. For the present data, where particle size and distance distributions interfere, the values obtained for R_G may only be taken as a very rough estimate.

A scaling analysis was tried for all aging sequences with all three characteristic lengths. The results for aging at 853 K are shown in Fig. 4. Scaling is observed to hold well for all aging times if $M_1^{-1}(t)$ is used for $L(t)$. $F(x)$ is roughly the same at 813 and 853 K, while a different
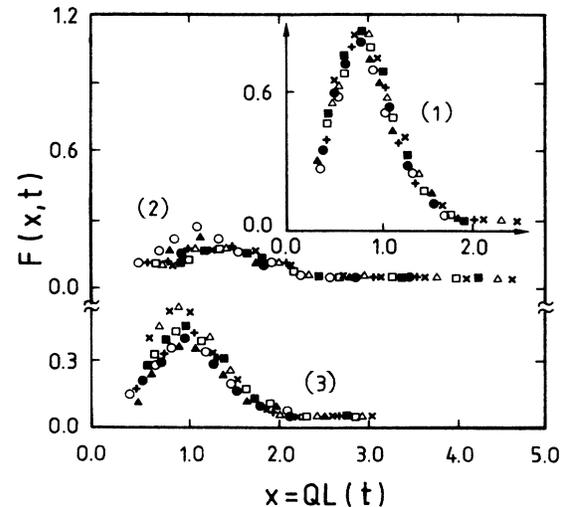

FIG. 4. Scaling analysis for the sample aged at 853 K for various aging times. O: Aged for 46 min; ▲: 72 min; ●: 101 min; +: 169 min; □: 253 min; ■: 337 min, △: 422 min; ×: 506 min. The scaling lengths are: (1) M^{-1}; (2) R_G; (3) Q_M^{-1}.

shape of $F(x)$ at 773 K may indicate another mechanism [$M_1^{-1}(t)$ itself is also time invariant]. At 813 and 853 K, $M_1^{-1}(t)$ varies according to a power law, $\propto t^a$, with $a \cong 0.2$. For the coarsening regime, $a = 0.33$ is expected,[4,5] at least for stress-free systems. A reduction of the exponent in the present alloy may be caused by strong coherency stresses (due to the large lattice mismatch between matrix and precipitate), as indicated by recent theoretical studies.[19,20]

*Present address: Institut für Festkörperphysik, Universität Wien, Boltzmanngasse 5, A-1090 Wien, Austria.

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