Temporal evolution of the nanostructure and phase compositions in a model Ni–Al–Cr alloy

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Abstract

In a Ni-5.2 Al-14.2 Cr at.% alloy with moderate solute supersaturations and a very small γ/γ' lattice parameter misfit, the nanostructural and compositional pathways during $\gamma'(L1_2)$ precipitation at 873 K are investigated using atom-probe tomography, conventional transmission electron microscopy, and hardness measurements. Nucleation of high number densities ($N_v > 10^{23} \text{ m}^{-3}$) of solute-rich precipitates (mean radius = $\langle R \rangle = 0.75 \text{ nm}$), with a critical nucleus composition of Ni-18.3 $\pm$ 0.9 Al-9.3 $\pm$ 0.7 Cr at.%, initiates between 0.0833 and 0.167 h. With increasing aging time (a) the solute concentrations decay in spheroidal precipitates ($\langle R \rangle < 10 \text{ nm}$); (b) the observed early-stage coalescence peaks at maximum N_v in coincidence with the smallest interprecipitate spacing; and (c) the reaction enters a quasi-stationary regime where growth and coarsening operate concomitantly. During this quasi-stationary regime, the γ (face-centered cubic)-matrix solute supersaturations decay with a power-law dependence of about $-1/3$, while the dependencies of $\langle R \rangle$ and N_v are 0.29 ± 0.05 and -0.64 ± 0.06 at a coarsening rate slower than model predications. Coarsening models allow both equilibrium phase compositions to be determined from the compositional measurements. The observed early-stage coalescence is discussed in further detail.

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1. Introduction

Many technologically important properties of alloys, such as their mechanical strength, creep resistance, and magnetic properties, are controlled by the presence of nanometer-sized precipitates of a second phase. In the solid state, the process of phase separation or decomposition may occur by homogeneous nucleation and growth of the second-phase precipitates with the same crystal structure (except for a possible difference in internal order) and a dif-

ferent composition than the solid-solution matrix. The system may also accommodate lattice parameter misfits between the two phases of up to several percent or more. A recent review of homogeneous precipitation in solid/solid phase transformations [1] outlines the majority of experimental work to date, as well as the pertinent theoretical and modeling considerations. Due to the technological importance of commercial alloys, model Ni-based alloys have warranted extensive investigation in the earliest stages of phase separation. This is particularly true for Ni–Al alloys, where the governing thermodynamics can be assessed in a fairly straightforward manner, and studied by small-angle and wide-angle neutron scattering [2,3], atom-probe field-ion microscopy [4], conventional transmission electron microscopy (CTEM) [5,6], and high-resolution electron microscopy (HREM) [7]. Due to the inadequate spatial and analytical resolution and other

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experimental limitations of these techniques, understanding of the earliest stages of decomposition is still incomplete. In particular, the nucleation of a new phase, its compositional evolution, and the concomitant kinetic pathways are incompletely understood.

Due to their excellent mechanical and physical properties at elevated temperatures, Ni-based superalloys based on Ni–Al–Cr compositions are technologically important alloys for use in both land based and aeronautical turbine engines [8]. Their strength at high temperatures is a direct consequence of the presence of coherent, elastically hard L_{12} -ordered precipitates of $Ni_3(Al_xCr_{1-x})$ (γ') in a face-centered cubic (fcc) chromium-rich solid solution (γ). In the γ' -phase (L_{12}), mixed planes of Ni, Al, and Cr alternate with nearly pure Ni planes along the $\langle 100 \rangle$ -type and $\langle 110 \rangle$ -type directions. The addition of Cr to the binary Ni–Al system reduces significantly the lattice parameter misfit between the γ - and γ' -phases, which in turn decelerates the coarsening kinetics. In certain Ni–Al–Cr alloys, the γ' -precipitates are nearly misfit free [9] and remain almost spherical or spheroidal to fairly large dimensions [10], making such a system amenable to comparison with classic treatments of nucleation, growth, and coarsening, which frequently assume a spherical stress-free precipitate/matrix interface. This is in contrast to binary Ni–Al alloys, where appreciable lattice parameter misfit gives rise to cuboidal-shaped precipitates [11].

Atom-probe tomography (APT) is a three-dimensional (3D) imaging technique that offers a high degree of analytical sensitivity with sub-nanometer spatial resolution with the atom-by-atom reconstruction of a volume of material, typically 10^4 or 10^6 nm³ for a conventional APT or local electrode atom-probe (LEAP) tomographic analysis, respectively. The seminal research of Schmuck et al. and Pareige et al. [12,13] demonstrates that experimental APT observations, in conjunction with lattice kinetic Monte Carlo (LKMC) simulations, yields a detailed atomic-scale picture of the early-stage decomposition of a model Ni–Al–Cr alloy. Applying this combined approach, our research efforts [14–19] focus on the genesis of the γ' -phase and its nanostructural and compositional evolution in a nearly identical Ni–Al–Cr alloy, Ni-5.2 Al-14.2 Cr at.%, containing low to moderate solute supersaturations, as it decomposes isothermally at 873 K. In this article, the APT characterization of the γ' -phase morphological development, phase composition evolution, and nanostructural evolution demonstrates that the transformation initiates by nucleation and growth and with increasing aging time enters a quasi-steady-stationary regime, where growth and coarsening are concomitantly operating. The experimental analyses presented permit the composition and radius of the critical nucleus, the equilibrium solvus-line compositions, and the three classic temporal power-law exponents for coarsening to be determined; the latter is compared to extant models of coarsening.

In an analytical model of multi-component coarsening, Umantsev and Olson [20] were the first to demonstrate that

independent of the number of components the exponents of the temporal power laws are the same as for a binary alloy (Lifshitz–Slyozov–Wagner model); with only the coarsening rate constants of the time-dependent power laws differing. Several models for the coarsening kinetics for multi-component systems remove the restriction of dilute-solution thermodynamics [20–24]. Only the model of Kuehmann and Voorhees (KV) [21] for isothermal coarsening in ternary alloys includes, however, the effects of capillarity on the precipitate composition, such that both the matrix and precipitate compositions can deviate from their equilibrium thermodynamic values. The KV model is valid for an extremely small volume fraction, ϕ , in the quasi-stationary-state regime, assuming a stress-free geometry. In the quasi-stationary limit, $t \rightarrow \infty$, the exponents of the power-law temporal dependencies for the average precipitate radius, $\langle R(t) \rangle$, the precipitate number density, N_v , and the matrix supersaturation of each solute species i , ΔC_i^γ , derived for the KV model are:

$$\langle R(t) \rangle^3 - \langle R(0) \rangle^3 = Kt \quad (1)$$

$$N_v \cong \frac{\phi^{eq}}{4.74K} t^{-1} \quad (2)$$

and

$$\Delta C_i^\gamma = \langle C_i^{\gamma,ff}(t) \rangle - C_i^{\gamma,eq}(\infty) = \kappa_i t^{-1/3} \quad (3)$$

where K and κ_i are coarsening rate constants for $\langle R(t) \rangle$ and ΔC_i^γ , respectively; $\langle R(0) \rangle$ is the average precipitate radius at the onset of coarsening; ϕ^{eq} is the equilibrium precipitate volume fraction; and ΔC_i^γ is the difference between the matrix concentration in the far-field matrix, $\langle C_i^{\gamma,ff}(t) \rangle$, and the equilibrium solute-solubility, $C_i^{\gamma,eq}$.

2. Experimental

High-purity constituent elements (Ni, 99.97 wt.%; Al, 99.98 wt.%; and Cr, 99.99 wt.%) were induction melted under an Ar atmosphere to minimize oxidation, and then chill cast in a 19 mm diameter copper mold to produce master ingots. The overall alloy composition, C_o , was determined to be 80.5 Ni-5.2 Al-14.2 Cr at.% employing inductively coupled plasma atomic emission spectroscopy. To ensure chemical homogeneity, cast ingots, consisting of coarse (0.5–2 mm diameter), equiaxed, and twinned grains [25], were homogenized at 1573 K for 24 h. Subsequently, the temperature was decreased to 1123 K and the ingot was held for 3 h in the γ (fcc)-phase field. By virtue of the smaller undercooling, this heat treatment aimed to reduce the concentration of quenched-in vacancies and suppress γ' (L_{12}) precipitation during the water quench to room temperature. As-quenched sections were aged at 873 K for times ranging from essentially zero (the as-quenched state) to 1024 h, and then cut into blanks ($0.25 \times 0.25 \times 10$ mm³) for APT specimens and sheets ($10 \times 19 \times 0.25$ mm³) for CTEM specimens with electrode discharge machining.

CTEM specimens were prepared from 3 mm discs ground mechanically to 150 μm thickness, employing standard electropolishing methods at 233 K with a solution of 8 vol.% perchloric acid and 14 vol.% 2-butoxyethanol in methanol at 10–12 Vdc. CTEM experiments [25,26] were performed with a Hitachi 8100 instrument operated at 200 kV, where ordered γ' -precipitates were imaged using a low-index superlattice reflection in a two-beam dark-field condition. APT specimens were prepared by a two-step electropolishing procedure: (i) 10 vol.% perchloric acid in acetic acid at 10–15 Vdc to thin uniformly the APT specimen blank and (ii) 2 vol.% perchloric acid in 2-butoxyethanol at 15 Vdc and reduced incrementally to 3 Vdc to create a necked region and refine the sharp end form. Vickers microhardness at 500 g load sustained for 5 s was measured on mounted samples polished to 1 μm . The average value of 15 independent measurements made on several grains was determined.

APT and field-ion microscopy (FIM) experiments [25,26] were performed using conventional APT [27,28] and an Imago Scientific Instrument's LEAP tomograph [29]. Prior to conventional APT analysis, specimens were imaged at 40–50 K with FIM at background gauge pressures of neon that varied from 6.7×10^{-4} to 2.6×10^{-3} Pa (5×10^{-6} to 2×10^{-5} torr). As shown in Fig. 1, FIM imaging reveals a prominent pole structure, which allowed the conventional APT analyses (typical region of ion detection denoted with dashed lines) to be aligned near a 001-crystallographic pole; this micrograph shows that the γ' -precipitates

are not visually distinguishable from the γ -matrix by image contrast. The lack of image contrast is consistent with the similar field-ionization and field-evaporation behavior of the γ - and γ' -phases. APT data collection was performed at a specimen temperature of 40.0 ± 0.3 K, a voltage pulse fraction (pulse voltage/steady-state direct current voltage) of 19%, a pulse frequency of 1.5 kHz (conventional APT) or 200 kHz (LEAP tomograph [29]), and a background gauge pressure of $<6.7 \times 10^{-8}$ Pa (5×10^{-10} torr). The average detection rate in the area of analysis ranged from 0.011 to 0.015 ions per pulse for conventional APT and from 0.04 to 0.08 ions per pulse for the LEAP tomographic analyses.

Three-dimensional atom-by-atom reconstructions of the analyzed volumes were generated utilizing ADAM 1.5 [30], a data analysis program developed at Northwestern University specifically for APT data. APT alignment of a specimen near the 001-crystallographic pole permits the reconstruction depth to be scaled to 001 planes, whose interplanar spacing is a known quantity, while the lateral dimensions are scaled with a reduced packing density ($83.6 \text{ atoms nm}^{-3}$ multiplied by the instrumental ion detection efficiency of 60%) leading to scaling errors of about 5 and 10% in the depth and lateral dimensions, respectively [25]. Consistent with the lack of image contrast between the γ - and γ' -phases in Fig. 1, the absence of large density fluctuations between the reconstructed phases demonstrates that the field-evaporation behavior of the two phases is similar. The γ/γ' interfaces are delineated with 9 at.% Al isoconcentration surfaces (approximately the mid-point value between bulk compositions of γ and γ') calculated with efficient sampling procedures [31] and parameters [25] that optimize the statistical noise and reduce positional errors. Employing this isoconcentration surface procedure, γ' -precipitates with radii (determined from the volume-equivalent radius of the best-fit ellipsoid [25]) as small as 0.45 nm (20 detected atoms) are resolved. Fewer atoms than the number expected for $R = 0.45$ nm are detected because the detection efficiency is $\sim 60\%$. The arithmetic mean of the measured volume-equivalent radii for only single γ' -precipitates, i.e., non-coalesced precipitates, contained fully within the volume, is used to calculate $\langle R \rangle$ for each aging time.

The precipitated volume fraction, ϕ , is determined directly from the ratio of the total number of atoms contained within the isoconcentration surfaces to the total number of atoms collected. Using a direct counting method, the precipitate number density, N_v , is determined by the number of γ' -precipitates contained in the APT reconstructed volumes, utilizing the following conventions: (a) a single precipitate contained fully within the volume contributes one; (b) a single precipitate contained partially within the volume contributes 0.5; and (c) a coalesced pair contained fully within the volume contributes two to the total N_v count. The same conventions are employed in the determination of the percentage of precipitates interconnected by necks, f . Assuming a regular simple cubic

Fig. 1. FIM image of a Ni-5.2 Al-14.2 Cr at.% specimen aged at 873 K for 256 h exhibiting a prominent pole structure and no discernable image-contrast differences between the γ - and γ' -phases. The dashed lines approximate the area of ion detection during conventional APT analyses, which are aligned near a 001 crystallographic pole. The ion detection area for LEAP tomograph analyses is approximately half the area of this FIM image. The Ni-5.2 Al-14.2 Cr at.% specimen displayed was imaged with 3.9×10^{-4} Pa (3×10^{-6} torr) gauge pressure of Ne at a specimen voltage of 12,708 Vdc and specimen temperature of 40 K.

Fig. 2. Horizontal solid lines mark the average core composition of the γ' -precipitates (left) and the far-field composition of the γ -matrix (right) measured from a proximity histogram composition profile [33] obtained from APT images of Ni-5.2 Al-14.2 Cr at.% specimens aged for 4 h at 873 K (Table 2). Profiles from three separate specimens analyzed with APT were combined to obtain this profile, which originates from γ/γ' interfaces of 173.5 precipitates ($\langle R \rangle = 1.27 \pm 0.21$ nm, Table 1) averaged over all crystallographic directions. The inset demonstrates the analytical sensitivity of this method; note the slight depletion of Al adjacent to the γ/γ' interface. The Al depletion arises from a chemical gradient associated with diffusion-limited growth, which is transient [15].

lattice array of γ' -precipitates, the average edge-to-edge interprecipitate spacing, $\langle \lambda_{e-e} \rangle$, is given by:²

$$2 \cdot \left[\left(\frac{4}{3} \pi \cdot N_v \right)^{-1/3} - \langle R \rangle \right] \quad (4)$$

Standard errors, σ , for $\langle R \rangle$, N_v , ϕ , f , and $\langle \lambda_{e-e} \rangle$ are calculated taking into account the counting statistics and reconstruction scaling errors [25] using standard error propagation methods [32].

Phase compositions in the γ -matrix far-field and γ' -precipitate core are obtained from the proximity histogram compositional profiles [33], which display the average concentrations in shells of thickness 0.25 nm at a given specified distance from the γ/γ' interfaces (9 at.% Al isoconcentration surfaces) (Fig. 2). This is accomplished by determining the number of atoms of each element within the shells associated with the plateau region of the composi-

tional profile for a given phase, which is marked with horizontal solid lines in Fig. 2 and is delineated by a visual assessment of the error in compositional measurements. Following Refs. [12,34], all reported values of composition were systematically corrected for preferential elemental loss of Ni and Al [25]. The standard error, σ , is calculated from uncorrected elemental concentrations, C_i , of component i using $\sqrt{C_i(1 - C_i)/N}$, where N is total number of atoms within the relevant volume. The temporal evolution of the proximity histogram compositional profiles demonstrates that a gradual gradient in Cr across the core region persists for $t \leq 64$ h [15], where Fig. 2 shows these gradients for specimens aged for 4 h. Since the compositional profile for Cr does not exhibit a plateau value for the precipitate phase, the precipitate core composition assessment is based on the plateau in the Al profile.

3. Results

At 873 K, a Ni-5.2 Al-14.2 Cr at.% solid solution contains low to moderate solute supersaturations. The lattice parameters, a , for the equilibrium phases at 873 K are estimated to be 0.3554 ± 0.0001 nm and 0.3552 ± 0.0001 nm for the γ' - and γ -phases, respectively, based on room-temperature X-ray diffraction measurements on similar Ni–Al–Cr alloys [9,10]. This results in a lattice parameter misfit, δ , estimate of 0.0006 ± 0.0004 , where $\delta = (a' - a'')/[0.5 \cdot (a' + a'')]$, which is very close to zero.

3.1. Morphological development

Spheroidal γ' -precipitates, which are nanometer-sized ($R \geq 0.45$ nm), are initially detected at $t = 0.167$ h with the isoconcentration surface analyses. In Fig. 3, a $12 \times 5 \times 2$ (120) nm³ partial volume from a conventional APT analysis along a [001]-direction displays a single γ' -precipitate,

Fig. 3. Al and Cr atoms in a $12 \times 5 \times 2$ nm³ (120 nm³) partial volume from a specimen aged for 0.167 h, displayed in off-white and dark-gray, are enlarged in the γ' -precipitate ($R = 0.8$ nm) to emphasize the resolved {002} superlattice planes perpendicular to the [001] analysis direction. The γ/γ' interface is delineated in gray with a 9 at.% Al isoconcentration surface. The time 0.167 h marks the first aging time when γ' -precipitation is detected in Ni-5.2 Al-14.2 Cr at.% using an APT direct lattice space reconstruction. Approximately 2/3 of the γ' -precipitate volume is imaged, and the full precipitate contains 109 detected atoms: 78 Ni (not displayed), 21 Al, and 10 Cr.

² For a regular simple cubic lattice array, $\langle \lambda_{e-e} \rangle$ is equal to $2 \cdot (L/2 - \langle R \rangle)$, where L is the lattice parameter of the array. The number density, N_v , is equal to the reciprocal of the unit volume occupied by a single precipitate in the array. It is worth noting that the unit volume is often approximated as a cube with a volume of L^3 . This approximation is incorrect because it breaks the radial symmetry of the 3D structure; therefore, we approximate the unit volume as the volume of a lattice-enclosed sphere $(4/3)\pi(L/2)^3$. Eq. (4) follows accordingly by direct substitution.

$R = 0.8$ nm, from a specimen aged for 0.167 h. As with all the analyses in this article, the γ/γ' interface is delineated with a 9 at.% Al isoconcentration surface. This precipitate's Al-rich $\{200\}$ L1₂-superlattice planes ($2d_{200} = 0.3554$ nm) are clearly resolved. The distribution of Al atoms (off-white circles) and Cr atoms (dark-gray circles) in Fig. 3 provides direct visual evidence for phase separation and demonstrates that APT positions atoms with sub-nanometer resolution.

Microhardness provides an indirect measure of the precipitation sequence through strength changes, which is a function of the precipitates' $\langle R \rangle$ and N_v values. Fig. 4 displays the evolution of the microhardness as a function of aging time at 873 K. Prior to 1 h, the microhardness is constant (1.25 GPa), after which it monotonically increases, reaching a value of 2.25 GPa at the final aging time of 1024 h. CTEM imaging demonstrates that a high N_v of γ' -precipitates are uniformly and randomly distributed in a specimen aged 1024 h (Fig. 5). At these large N_v and small $\langle R \rangle$ (~ 8 nm) values, N_v is determined more accurately from APT images than from CTEM images because precipitate overlap and truncation effects associated with projection imaging is severe with the latter technique. However, CTEM imaging confirms that the γ' -precipitates remain spheroidal to the longest aging time, 1024 h, with no evidence of coherency loss.

In this alloy, where the equilibrium phase partitioning of solute is not particularly strong at 873 K, it is useful to omit the atoms within the APT image and to visualize the precipitates with isoconcentration surfaces (particularly when $\langle R \rangle < 1$ nm). Fig. 6 presents the full nanostructural evolution of the γ' -precipitation process at 873 K for aging times up to 1024 h within a series of APT volumes: $10 \times 10 \times 25$ (2500) nm³ subsets each containing 125,000 atoms. Qualitatively, both the N_v and $\langle R \rangle$ values increase with aging time until 4 h, after which the precipitates continue to coarsen as evidenced by continued increase in $\langle R \rangle$ and concomitant decrease in N_v . The morphology of the γ' -precipitates is a mixture of individual spheroidal precipitates and precipitates interconnected by necks. The incidence of coalesced

Fig. 4. Vickers microhardness versus aging time at 873 K for Ni-5.2 Al-14.2 Cr at.%.

Fig. 5. Centered superlattice reflection dark-field image of γ' -precipitates in a Ni-5.2 Al-15.2 Cr at.% sample aged for 1024 h at 873 K reveals a uniform distribution of spheroidal γ' -precipitates at a high number density, $(1.1 \pm 0.6) \times 10^{23} \text{ m}^{-3}$. This image was recorded near the $[001]$ zone axis using a 200 superlattice reflection.

Fig. 6. Temporal evolution of the γ' -phase nanostructure in Ni-5.2 Al-14.2 Cr at.% specimens, aged at 873 K, is revealed within a series of APT images. Each parallelepiped is a $10 \times 10 \times 25$ nm³ (2500 nm³) subset of an analyzed volume and contains approximately 125,000 atoms per parallelepiped. The γ/γ' interfaces are delineated in gray with 9 at.% Al isoconcentration surfaces and individual atoms are not exhibited for the sake of clarity.

triplet precipitates and higher order events are rare. In Fig. 7(a), the Al-rich γ' -regions and Cr-rich γ -regions are clearly visualized in the reconstructed volume of the sample aged for 4 h. The corresponding γ/γ' interfaces within this volume (Fig. 7(b)) show that a high fraction of the γ' -precipitates are interconnected by necked regions. Moreover, examination of the Al and Cr atoms in three γ' -precipitate pairs (Fig. 7(c)), within the volume, demonstrate that the Al-rich $\{002\}$ superlattice planes extend across the necked

Fig. 7. A $15 \times 15 \times 30 \text{ nm}^3$ (6750 nm^3) subset of an APT reconstructed volume of Ni-5.2 Al-14.2 Cr at.% aged at 873 K for 4 h displaying (a) Al and Cr atoms and (b) the γ' -precipitates delineated by 9 at.% Al isoconcentration surfaces. (c) The Al and Cr atoms within three γ' -precipitate pairs, labelled in (b), demonstrate that the Al-rich $\{002\}$ superlattice planes extend across the necked regions without APBs.

region without the presence of an anti-phase boundary (APB). The coarser γ' -phase nanostructure at 256 h is imaged with both conventional APT and LEAP tomography (Fig. 8). The conventional APT analysis ($16 \times 16 \times 195$ ($49,920 \text{ nm}^3$)) partially intersects 23 γ' -precipitates in 36 h of analysis and is composed of 1.8×10^6 atoms. The LEAP tomographic analysis ($86 \times 86 \times 63$ ($465,948 \text{ nm}^3$)) intersects fully 50 γ' -precipitates and partially 20 γ' -precipitates detecting 9.8×10^6 atoms after 0.8 h of collecting data. Only the Al (red) and Cr (blue) atoms in the γ' -precipitates are displayed within these volumes, allowing the dense distribution of γ' -precipitates to be identified in 3D. Three-dimensional imaging does not suffer from the same projection effects associated with CTEM imaging, which is a 2D projection of a 3D object. As seen in Fig. 8, conventional APT is, however, limited to smaller analyzed volumes, typically $15 \times 15 \times 100$ ($22,500 \text{ nm}^3$). Alternatively, LEAP tomographic analyses are capable of analyzing greater than $100 \times 100 \times 100$ (10^6 nm^3) in a significantly shorter time.

3.2. Temporal evolution of the nanostructural properties

The nanostructural properties, $\langle R \rangle$, N_v , ϕ , f , and $\langle \lambda_{c-e} \rangle$, determined from APT reconstructed volumes for the iso-

Fig. 8. Specimens of Ni-5.2 Al-14.2 Cr at.% aged at 873 K for 256 h were analyzed with (a) conventional APT and with (b) LEAP tomography. The $16 \times 16 \times 195 \text{ nm}^3$ ($24,320 \text{ nm}^3$) and $86 \times 86 \times 63 \text{ nm}^3$ ($464,948 \text{ nm}^3$) volumes contain $\sim 1.8 \times 10^6$ and 9.8×10^6 atoms, respectively. Only Al (red) and Cr (blue) atoms within γ' -precipitates are displayed for the sake of clarity.

thermal transformation at 873 K are summarized in Table 1. These measurements are based on several to hundreds of analyzed precipitates, N_{ppt} (Table 1).

3.2.1. Nucleation and growth of the γ' -precipitates ($t \leq 4 \text{ h}$)

At $t = 0.167 \text{ h}$, $\langle R \rangle$, and ϕ are determined to be 0.74 nm and 0.11%, respectively. As shown in Fig. 9, a sharp rise in the value of N_v (filled circles) is observed between 0.167 and 0.25 h, while the value of $\langle R \rangle$ (open circles) is constant (0.75 nm), which is an indication that nucleation of stable γ' -precipitates is the dominant mechanism at early aging times. This furthermore demonstrates experimentally that an upper bound to the critical radius of nucleation is approximately 0.75 nm. Stability of the γ' -nuclei can be assessed directly from LKMC simulations for the same aging conditions [17]. The LKMC simulations indicate that when γ' -precipitates contain approximately 40 atoms they become resistant to dissolution, which corresponds to a critical radius of nucleation, R^* , value of 0.485 nm, which is 35% smaller than our upper bound of 0.75 nm. Analysis of the APT volumes with isoconcentration surfaces (Fig. 6) resolves γ' -precipitates as small as 0.45 nm, $\sim R^*$.

Table 1

Temporal evolution of the nanostructural properties^a of a Ni-5.2 Al-14.2 Cr at.% alloy aged at 873 K for different times

t (h)	N_{ppt}^b	$\langle R \rangle \pm \sigma$ (nm)	$N_v \times 10^{24} \pm \sigma$ (m ⁻³)	$\phi \pm \sigma$ (%)	$f \pm \sigma$ (%)	$\langle \lambda_{e-e} \rangle^c \pm \sigma$ (nm)
0.167	7.5	0.74 ± 0.24	0.36 ± 0.13	0.11 ± 0.04	ND ^d	16.0 ± 2.8
0.25	74	0.75 ± 0.14	2.1 ± 0.4	0.55 ± 0.06	9 ± 3	8.2 ± 0.8
1	100	0.89 ± 0.14	2.5 ± 0.5	2.33 ± 0.23	24 ± 6	7.4 ± 0.8
4	173.5	1.27 ± 0.21	3.2 ± 0.6	5.2 ± 0.4	30 ± 4	5.9 ± 0.8
16	101	2.1 ± 0.4	1.49 ± 0.27	8.8 ± 0.9	21 ± 4	6.6 ± 1.1
64	46	2.8 ± 0.6	0.49 ± 0.17	10.0 ± 1.5	13 ± 5	10.1 ± 2.9
256 ^d	81 ^d	4.1 ± 0.8	0.24 ± 0.04	13.3 ± 1.5	2.5 ± 1.7	11.9 ± 2.1
1024	6	7.7 ± 3.3	0.11 ± 0.06	15.6 ± 6.4	ND ^e	11 ± 7

^a Mean radius of γ' -precipitates ($\langle R \rangle$), the number density (N_v), precipitated volume fraction (ϕ), percentage of precipitates interconnected by necks (f), average edge-to-edge interprecipitate spacing ($\langle \lambda_{e-e} \rangle$), and their standard errors (σ).

^b For the number of precipitates analyzed, N_{ppt} , single precipitates intersected partially by the sample volume contribute 0.5 to this quantity, while a fully enclosed precipitate pair connected by a neck contributes 2.

^c Calculated from $\langle R \rangle$ and N_v measurements employing Eq. (4).

^d For the 256 h aging state, 11 and 70 precipitates were analyzed with conventional APT and a LEAP tomograph, respectively.

^e ND = not detected.

Fig. 9. Temporal evolution of the γ' -precipitate volume fraction (ϕ), number density (N_v), and average radius ($\langle R \rangle$) in Ni-5.2 Al-14.2 Cr at.% aged at 873 K as determined by structural measurements from APT data (Table 1). The ϕ^{eq} value, $15.6 \pm 0.4\%$ is based on a lever-rule determination from the equilibrium phase compositions presented in Table 2.

Therefore, unstable embryos do not contribute significantly to the determination of $\langle R \rangle$. Although initially at $t = 0$ h the Cr atoms in the as-quenched alloy are randomly distributed, a distribution of congruent Ni_3Al short-range order (SRO) domains, $\langle R \rangle \approx 0.6$ nm, results from Al diffusion during post-homogenization quenching [16]. Albeit based on only two experimental data points, the sharp linear slope of the N_v profile, $(5.9 \pm 1.7) \times 10^{21} \text{ m}^{-3} \text{ s}^{-1}$, when $\langle R \rangle$ is a constant 0.75 nm may be considered an estimate of a quasi-stationary-state nucleation current, J_{SS}^* . The N_v intercept on the abscissa is an estimate of the nucleation incuba-

tion time, τ , of 540 ± 120 s; this behavior is similar to that described by classic nucleation theory [35–37]. In addition to quenched-in SRO domains, diffusional field overlap associated with chemical transients that extend 3 nm from γ/γ' interface (see Fig. 2) [15] influence early-stage decomposition. Therefore, a highly detailed comparison to J_{SS}^* and τ , with values determined by classic stationary-state theory of nucleation is probably not instructive. Following the sharp increase in N_v to $(2.1 \pm 0.4) \times 10^{24} \text{ m}^{-3}$, its value increases slowly between 0.25 and 4 h to a maximum value of $(3.2 \pm 0.6) \times 10^{24} \text{ m}^{-3}$. New nuclei are formed during this time period at a rate that is significantly slower than during quasi-stationary-state nucleation, while stable nuclei grow as both $\langle R \rangle$ and ϕ are increasing.

The experimental nanostructural temporal evolution has been reproduced with recent LKMC simulations using the same aging conditions [17]. These LKMC simulations verify that coagulation ($t \leq 4$ h) and coalescence without significant precipitate migration is responsible for the interconnected γ' -phase nanostructure that is observed rather than precipitate splitting, which can result from growth instabilities or elastically induced splitting [38]. In the context of this article, coagulation is defined as the discrete instance when neighboring precipitates join, while coalescence is the growth period that follows coagulation during which joined precipitates retain a concave neck. The 3D APT imaging allows the percentage of γ' -precipitates interconnected by necks, f , to be experimentally quantified (Fig. 10). Interconnected precipitates are first detected with APT after 0.25 h of aging with an f value of $9 \pm 3\%$. This is near the end of the quasi-steady-state nucleation regime when $\langle R \rangle = 0.75$ nm. With increasing time, f increases continuously and reaches a maximum value of $30 \pm 4\%$ at 4 h, which corresponds simultaneously to the peak N_v value of $(3.2 \pm 0.6) \times 10^{24} \text{ m}^{-3}$, the smallest $\langle \lambda_{e-e} \rangle$ value of 5.9 ± 0.8 nm, and an $\langle R \rangle$ value of 1.27 ± 0.21 . This continuous increase in f between 0.25 and 4 h corresponds to the time scale where coagulation events occur, in agreement with the LKMC simulation observations.

Fig. 10. Percentage of γ' -precipitates interconnected by necks (f) reaches a maximum value at 4 h, which corresponds to a minimum value in the average edge-to-edge interprecipitate spacing, $\langle\lambda_{e-e}\rangle$ (Table 1), of 5.9 ± 0.8 nm.

3.2.2. Growth and coarsening of the γ' -precipitates ($t > 4$ h)

The maximum value of N_v (3.2 ± 0.6) $\times 10^{24}$ m^{-3} , is achieved at approximately 4 h of aging, after which the transformation enters a regime with a constant temporal power-law exponent of -0.64 ± 0.06 , which disagrees with the -1 prediction for Ostwald ripening in multi-component alloys (Eq. (2)). During this regime, growth and coarsening operate concomitantly as the value of ϕ steadily increases towards its equilibrium value of 15.6% after 256 h of aging (upper panel in Fig. 9). Assuming $\langle R \rangle^3$ evolves linearly with time, the coarsening relationships demonstrate that N_v will not decay as t^{-1} when ϕ is less than its equilibrium value (i.e., when the transformation is not complete) [39]. The temporal power-law exponent for $\langle R \rangle$ is 0.29 ± 0.05 for $t \geq 1$ h, which is in approximate agreement, but not exact, with the predicted value of $1/3$ for Ostwald ripening in multi-component alloys (Eq. (1)). The approximate agreement with $1/3$ indicates the transformation is primarily diffusion-limited. The temporal power-law exponent prediction for $\langle R \rangle$ of $1/2$ for diffusion-limited growth [1,40] is not, however, observed, contrary to an earlier APT investigation [12,13]. A linear regression analysis of $\langle R \rangle^3$ for $t \geq 4$ h yields a coarsening rate constant, K , of $(8.8 \pm 3.3) \times 10^{-32}$ $\text{m}^3 \text{s}^{-1}$ and a reasonable value for $\langle R(0) \rangle$ of 0.97 nm; the latter corresponds to the time at which coarsening commences. After reaching a maximum value of $30 \pm 4\%$

at 4 h, f decreases toward zero, coagulation has terminated, and the decay after 4 h indicates γ' -precipitates in various stages of coalescence. No necks are detected in the 1024 h aging state; and the corresponding f -value is probably below the detection limit of conventional APT.

3.3. Temporal evolution of γ -matrix and γ' -precipitate composition

The compositions of both the γ - and γ' -phases evolve continuously with time (Table 2). Contrary to what is commonly assumed in most classic models for nucleation, growth, or coarsening, the γ' -precipitate composition in this alloy continues to evolve temporally from the first measured aging time. The γ' -precipitates' cores are supersaturated with Al (19.1 ± 2.8 at.%) and Cr (9.7 ± 2.1 at.%) at $t = 0.167$ h. These supersaturations decrease continuously and at 1024 h the γ' -precipitates contain 16.70 ± 0.29 at.% Al and 6.91 ± 0.20 at.% Cr. The Cr supersaturation in the γ' -precipitates is associated with kinetically trapped Cr in the nucleating and growing γ' -precipitates, which produces a gradual decrease in Cr concentration toward the core region [15]. The composition of the critical nucleus is estimated to be 72.4 $\pm$ 1.1 at.% Ni, 18.3 $\pm$ 0.9 at.% Al, and 9.3 $\pm$ 0.7 at.% Cr ($\text{Ni}_{0.724}\text{Al}_{0.183}\text{Cr}_{0.093}$), where these are lower bounds for the Al and Cr concentrations because this estimation is an average over the total distribution of γ' -precipitates for $t = 0.167$ and 0.25 h (where nucleation dominates the decomposition process). With increasing aging time, the far-field concentrations of Al in the γ -matrix decrease, while the Cr concentration increases (Table 2), characteristic of decreasing supersaturations as Al partitions to γ' -precipitates and Cr to the γ -matrix.

After 4 h, the temporal change in solute supersaturation in the γ -matrix is small ($d\Delta C/dt \rightarrow 0$) (Table 2), which implies that the system is entering a quasi-stationary-state regime for $t > 4$ h. Eq. (3) describes the time-dependent decay of the far-field concentrations toward the composition of a flat interface at infinite time. Fitting the matrix far-field concentration measurements ($t \geq 16$ h) to Eq. (3)

Table 2

Temporal evolution of the composition in the far-field $\gamma(\text{fcc})$ -matrix ($C_i^{\gamma,\text{ff}}$) and the $\gamma'(\text{L}_{12})$ -precipitates' core ($C_i^{\gamma'}$), and extrapolated ($t = \infty$) compositions at the phase boundaries (solvus lines) at 873 K

873 K t (h)	γ -Matrix (far-field)			γ' -Precipitates ^a (core)		
	$C_{\text{Ni}}^{\gamma} \pm 2\sigma$ (at.%)	$C_{\text{Al}}^{\gamma} \pm 2\sigma$ (at.%)	$C_{\text{Cr}}^{\gamma} \pm 2\sigma$ (at.%)	$C_{\text{Ni}}^{\gamma'} \pm 2\sigma$ (at.%)	$C_{\text{Al}}^{\gamma'} \pm 2\sigma$ (at.%)	$C_{\text{Cr}}^{\gamma'} \pm 2\sigma$ (at.%)
0.167	80.59 $\pm$ 0.09	5.19 $\pm$ 0.05	14.22 $\pm$ 0.08	71.3 $\pm$ 3.1	19.1 $\pm$ 2.7	9.7 $\pm$ 2.1
0.25	80.73 $\pm$ 0.09	5.07 $\pm$ 0.05	14.20 $\pm$ 0.08	72.6 $\pm$ 1.1	18.2 $\pm$ 0.9	9.2 $\pm$ 0.7
1	80.88 $\pm$ 0.10	4.75 $\pm$ 0.06	14.36 $\pm$ 0.09	73.4 $\pm$ 0.8	17.8 $\pm$ 0.6	8.8 $\pm$ 0.5
4	81.01 $\pm$ 0.15	3.97 $\pm$ 0.08	15.02 $\pm$ 0.14	74.3 $\pm$ 0.5	17.7 $\pm$ 0.4	8.0 $\pm$ 0.3
16	81.10 $\pm$ 0.06	3.61 $\pm$ 0.03	15.28 $\pm$ 0.06	75.48 $\pm$ 0.26	17.19 $\pm$ 0.23	7.33 $\pm$ 0.16
64	81.22 $\pm$ 0.07	3.45 $\pm$ 0.04	15.33 $\pm$ 0.07	75.7 $\pm$ 0.3	17.17 $\pm$ 0.28	7.16 $\pm$ 0.19
256 ^b	81.22 $\pm$ 0.07	3.30 $\pm$ 0.03	15.47 $\pm$ 0.07	75.95 $\pm$ 0.20	16.96 $\pm$ 0.17	7.08 $\pm$ 0.12
1024	81.16 $\pm$ 0.09	3.27 $\pm$ 0.04	15.57 $\pm$ 0.09	76.4 $\pm$ 0.3	16.70 $\pm$ 0.29	6.91 $\pm$ 0.20
∞	81.26 $\pm$ 0.18	3.13 $\pm$ 0.08	15.61 $\pm$ 0.18	76.5 $\pm$ 0.5	16.7 $\pm$ 0.4	6.77 $\pm$ 0.30

^a Precipitate composition is determined from an average of several to hundreds of precipitates (Table 1).

^b LEAP tomograph results are excluded from the compositional measurements due to a compositional dependence on crystallographic orientation [25].

Fig. 11. Double-logarithmic plot of the temporal evolution of the absolute value of the Al and Cr supersaturations in the γ -matrix (Eq. (3)) in Ni-5.2 Al-14.2 Cr at.% aged at 873 K.

yields the γ -phase boundary composition (Table 2) on the solvus line between the γ' -plus γ -phase field and the γ -phase field. The temporal evolution of the absolute values of ΔC_i^γ for $i = \text{Al}, \text{Cr}$ are presented in Fig. 11, where the $\Delta C_i^{\text{Al}}(t)$ values are positive and the $\Delta C_i^{\text{Cr}}(t)$ values are negative. Temporal power-law exponents are determined to be -0.33 ± 0.04 and -0.34 ± 0.07 for Al and Cr, respectively, which agree with the model exponent prediction of $-1/3$ (Eq. (3)), and marks the first observation in a ternary alloy where both temporal power-law exponents agree with the model's predictions. When both solute supersaturations in the matrix decay as $t^{-1/3}$, it is straightforward to show from the Gibbs–Thomson equation for the γ' -precipitate phase derived for ternary alloys [21] that a relationship analogous to Eq. (3) is also valid for the γ' -precipitate phase [19]. Therefore, the γ' -phase solvus line composition is accordingly determined (Table 2). The measured solute concentrations in the γ' -precipitates during the nucleation regime ($\langle R \rangle = 0.75 \text{ nm}$) are $\sim 2 \text{ at.}\%$ above their equilibrium values (Table 2), and the concentration amplitudes decay with time as the γ' -precipitates grow. This trend is consistent with the nucleation and growth mode of decomposition when capillarity is correctly taken into account [19].

4. Discussion

Although often treated as distinct processes, nucleation, growth, and coarsening can occur concomitantly as a precipitating phase evolves [1,36]. The correlation between the quantities N_v , ϕ , and $\langle R \rangle$ as they evolve temporally indicates the operative processes. Three regimes are experimentally identified for the Ni-5.2 Al-14.2 Cr at.% alloy by employing APT: (i) nucleation ($t = 0.167\text{--}0.25 \text{ h}$); (ii) concomitant nucleation and growth ($t = 0.25\text{--}4 \text{ h}$); and (iii)

concomitant growth and coarsening ($t > 4 \text{ h}$). An interesting aspect of this particular first-order phase transformation is the coagulation and coalescence of γ' -precipitates. The following discussion focuses on the origin of coagulation and coalescence and possible driving forces during early- to late-stage decomposition.

Although rare, the coalescence among coherent γ' -precipitates during precipitation in the absence of an external stress field has been reported in Ni–Al–Cr [41,42], Ni–Al–Mo [43], and Ni–Al–Co [44] alloys during the intermediate to late stages of coarsening for aging temperatures ranging from 750 to 850 °C and $\phi^{\text{eq}} > 35\%$. In the Ni–Al–Cr alloy studied, coagulation and coalescence between nanometer-sized precipitates occurs in the early stages of decomposition at small $\phi(t)$, for instance $\phi(t = 4 \text{ h}) = 5.2\%$, whereas after 4 h (the peak value of N_v) coagulation no longer occurs and the fraction, f , of coalesced γ' -precipitates decays with increasing aging time (Fig. 10). This marks the first direct-space evidence of coagulation and coalescence in the solid state during early-stage decomposition mediated by nucleation and growth. Indirect neutron scattering experiments suggest that this phenomenon may also be active in a Ni-13.2 Al at.% alloy aged at 823 K [2].

As noted, the highest observed percentage, $f = 30 \pm 4\%$, of the γ' -precipitates that are interconnected with necks corresponds to peak number density $(3.2 \pm 0.6) \times 10^{24} \text{ m}^{-3}$, after 4 h of aging, when $\langle R \rangle = 1.27 \pm 0.21 \text{ nm}$, $\phi = 5.2 \pm 0.4\%$, and $\langle \lambda_{\text{e-e}} \rangle = 5.9 \pm 0.8 \text{ nm}$ ($4.65\langle R \rangle$). We consider, hereafter, whether this observed f value may or may not be explained by simple geometric arguments (i.e., neighboring γ' -precipitates impinging during growth due to their proximity) alone without further consideration of the details of the diffusional processes. The L1_2 structure of the γ' -phase has four translational variants such that the coalescence among neighboring γ' -precipitates of different variants requires the formation of an APB. Since the lowest APB energy is for the $\{001\}$ -type plane, 104 mJ m^{-2} [45], which is four to five times greater than the experimentally determined γ/γ' interfacial free energy $(22\text{--}23) \pm 7 \text{ mJ m}^{-2}$ [19], averaged over all crystallographic directions, γ' -precipitates with different variants should not coalesce. Our geometric arguments assume that: (i) the establishment of the ordering variant during γ' -nucleation is not influenced by the variant neighbors in near proximity; (ii) γ' -precipitates do not change variants during growth (i.e., no precipitate migration); and (iii) coagulation among precipitates with different ordering variants does not occur. In a random distribution of nucleation events, no particular L1_2 variant would be favored, and each variant would have the same probability of occurrence, 25%, since there are four variants. Coagulation and coalescence depends strongly on the $\lambda_{\text{e-e}}$ values among neighboring precipitates. Therefore, only γ' -precipitates whose edges are within a critical distance (L^*) may coagulate and then coalesce. To predict f for a particular microstructure, it is convenient to use the average number of neighbors within L^* around a precipitate, $\langle \eta^* \rangle$, to describe the spatial arrangement of

precipitates. For spatial distributions corresponding to $\langle\eta^*\rangle = 1$,³ the predicted f value is equal to the variant percentage, 25% for L1₂, since on average each precipitate in the distribution has a single opportunity to coagulate and only neighbors with the same ordering variant coagulate and then coalesce. For distributions when $\langle\eta^*\rangle < 1$, there are fewer opportunities for coagulation. The predicted f value decreases accordingly and is equal to $\langle\eta^*\rangle$ multiplied by $f(\langle\eta^*\rangle = 1)$, where the latter quantity is 25% for L1₂. The value of $\langle\eta^*\rangle$ can exceed unity for densely packed distributions.

For specimens aged for 4 h, a direct quantitative determination of $\langle\eta^*\rangle$ from the observed λ_{c-e} distribution among the γ' -precipitates within the conventional APT datasets is not accurate due to volume truncation effects, as seen in Fig. 8(a) for the 256 h aging state. Assuming that the average diameter of γ' -precipitates during nucleation of 1.5 nm is a reasonable estimate for L^* and given that $\langle\lambda_{c-e}\rangle = 5.9$ nm for the 4 h aging state, the value of $\langle\eta^*\rangle$ is estimated to be approximately 0.25 from direct visual assessment of the spatial arrangement in the APT images (Fig. 6). This assessment corresponds to a predicted f -value of 7.5%, which is significantly smaller than the 30% that is observed experimentally. Therefore, the experimental observations cannot be explained solely by geometric arguments. This implies at least two possibilities operating solely or in concert: (i) nucleation is not random, that is, the resulting variant of a forming embryo is influenced during nucleation to match the variant of its neighbor (correlation) and/or (ii) the γ' -precipitates of initially different variants align prior to coalescence. The latter occurs possibly by a small translational and/or rotational movement of precipitates.

Sequeira et al. [43] suggest, for coarser microstructures ($\langle R \rangle > 85$ nm) in Ni–Al–Mo alloys, that coalescence is possibly driven by the removal of elastically strained matrix material between the γ' -precipitates. In our Ni–Al–Cr alloy, the small δ value of 0.0006 ± 0.0004 does not vary significantly over the range of evolving phase compositions [9]. Thus, for the small $\langle R \rangle$ values in our alloy the coherency strains are negligible. Furthermore, given that the γ' -precipitates that undergo coagulation and coalescence in our study are typically similar in diameter, the elastic strain field of each γ' -precipitate, which scales with the lattice parameter misfit and $\langle R \rangle^3$ [1], is accommodated by its neighbor. Therefore, elastic strain energy effects do not contribute significantly to the driving force for coagulation and coalescence in our experimental study, although such effects may play a more important role in systems with coarser microstructures and among precipitates more disparate in size. As the mechanism for coalescence in this Ni–Al–Cr alloy remains unresolved, further investigations employing LKMC simulations of the ordering variant

evolution and associated diffusional mechanisms are in progress.

The underlying mechanism for Oswald ripening is frequently assumed to be evaporation of single atoms from smaller precipitates, which diffuse through the matrix, via a random walk, and eventually condense on larger precipitates; this is the so-called evaporation–condensation mechanism. Models that consider diffusional interactions among precipitates during Oswald ripening, important in systems with a finite ϕ , establish that K along a given tie-line increases with increasing ϕ [46]. In an article published shortly after such models were first introduced, Chellman and Ardell [41] evaluated the available coarsening data at 1023 K along a γ plus γ' tie-line for four nearly misfit-free γ' -strengthened Ni–Al–Cr alloys [10,41,47] with increasing ϕ (0.23 to 0.42), and they found that within experimental error K does not vary with ϕ . They concluded that the ϕ independence of K is associated with the approximations used to solve the diffusion problems in these models, but they did not consider that diffusional processes may not be strictly governed by diffusion in the matrix [48]. For our alloy, using calculated intrinsic diffusivities in the γ -phase of $2.2 \times 10^{-20} \text{ m}^2 \text{ s}^{-1}$ for Al and $7.0 \times 10^{-21} \text{ m}^2 \text{ s}^{-1}$ for Cr [49,50], the calculated K values (Eq. (1)) of $5.6 \times 10^{-31} \text{ m}^3 \text{ s}^{-1}$ and $1.3 \times 10^{-30} \text{ m}^3 \text{ s}^{-1}$ without and with corrections for finite ϕ [25] are 7 to 15 times greater than our measured value of $(8.8 \pm 3.3) \times 10^{-32} \text{ m}^3 \text{ s}^{-1}$. The experimental observation of kinetically trapped Cr in the nucleating and growing γ' -precipitates [15] suggests that diffusional processes play an important role in the phase decomposition in this alloy. We attribute, therefore, our smaller measured K value to vacancy diffusion in both the γ -matrix and γ' -precipitates. At 873 K, the tracer diffusivities of Al and Cr in pure Ni₃Al are $2.7 \times 10^{-23} \text{ m}^2 \text{ s}^{-1}$ [51] and $4.0 \times 10^{-23} \text{ m}^2 \text{ s}^{-1}$ [52], respectively, which are approximately two orders of magnitude smaller than the solute diffusivities in the γ -matrix. It is therefore plausible that the invariance of K with respect to ϕ reported in Ref. [41], for γ' -strengthened Ni–Al–Cr alloys, is the result of two counteracting effects: (i) an acceleration in K with increasing ϕ associated with the increased diffusional interactions among γ' -precipitates and (ii) a deceleration in K with increasing ϕ associated with increasing diffusional processes in the γ' -precipitates. Therefore, the number of experimental alloys that actually satisfy completely the governing diffusion mechanisms assumed by the extant coarsening models may be limited.

5. Summary and conclusions

We studied in great detail the temporal evolution of the nanostructure and composition of a supersaturated Ni-5.2 Al-14.2 Cr at.% alloy undergoing a first-order phase transformation, $\gamma(\text{fcc}) \rightarrow \gamma(\text{fcc}) + \gamma'(\text{L1}_2)$, with a very small γ/γ' lattice parameter misfit value (0.0006 ± 0.0004), at 873 K for aging times up to 1024 h leading to the following conclusions:

³ An infinite number of spatial arrangements satisfies $\langle\eta^*\rangle = 1$. A special example of a distribution with $\langle\eta^*\rangle = 1$ is a volume where precipitates are grouped in distinct pairs with a constant spacing, such that the distribution of λ_{c-e} is a delta function with a value equal to or less than L^* .

- APT measurements (Table 1 and Fig. 9) of the number density, N_v , average precipitate radius, $\langle R \rangle$, and precipitate volume fraction, ϕ , on several to hundreds of γ' -precipitates permit us to identify three decomposition regimes: (i) nucleation ($t = 0.167$ – 0.25 h); (ii) concomitant nucleation and growth ($t = 0.25$ – 4 h); and (iii) concomitant growth and coarsening ($t > 4$ h). This allows the full range of decomposition processes to be investigated in great detail.
- The first evidence of γ' precipitation in APT images (Figs. 3, 6), with γ' -precipitates as small as $R = 0.45$ nm (20 detected atoms), occurs after aging for 0.167 h to a number density of $(3.6 \pm 1.3) \times 10^{23} \text{ m}^{-3}$. During γ' -phase nucleation ($t = 0.167$ – 0.25 h), the constant $\langle R = 0.75$ nm (Fig. 9) implies an upper bound to the critical radius for nucleation, R^* . The average measured composition, 72.4 ± 1.1 Ni– 18.3 ± 0.9 Al– 9.3 ± 0.7 Cr at.% ($\text{Ni}_{0.724}\text{Al}_{0.183}\text{Cr}_{0.093}$), is an estimate of the composition of the critical nucleus. The quasi-stationary-state nucleation current and incubation time are estimated to be $(5.9 \pm 1.7) \times 10^{21} \text{ m}^{-3} \text{ s}^{-1}$ and 540 ± 120 s, respectively, from a linear extrapolation of N_v measurements (Fig. 9).
- The peak number density of γ' -precipitates, $(3.2 \pm 0.6) \times 10^{24} \text{ m}^{-3}$, occurs at 4 h, and the first-order phase transformation enters a quasi-stationary-state regime between 4 and 16 h. In the quasi-stationary state, evaluated at $t \geq 16$ h, the temporal power-law dependence for $\langle R \rangle$ is 0.29 ± 0.05 and for N_v , it is -0.64 ± 0.06 (Fig. 9).
- A uniform distribution of spheroidal γ' -precipitates is retained out to $t = 1024$ h (Fig. 5). Three-dimensional imaging with APT (Figs. 6 and 7) demonstrates that the majority of the coherent γ' -precipitates are spheroidal. Throughout the phase transformation ($t = 0.25$ – 256 h), a fraction, f , of the γ' -precipitates are, however, in various stages of coagulation and coalescence (Fig. 10). The necked regions connecting γ' -precipitates do not contain APBs.
- A maximum f -value of $30 \pm 4\%$ after 4 h of aging coincides with the smallest edge-to-edge interprecipitate spacing, 5.9 nm, and is greater than geometric predictions for coalescence of L1_2 -ordering variants for the observed spatial distributions of the γ' -precipitates. Given the significant barrier (APB energy) to coagulation between γ' -precipitates of nonmatching variants, this high f -value implies that a small translational/rotational motion prior to coagulation is necessary for γ' -precipitates of nonmatching variants to join.
- Contrary to some classic treatments of nucleation, growth, and coarsening, the γ' -precipitate composition evolves temporally (Table 2), where both the Al and Cr concentrations in the γ' -precipitate cores decrease continuously toward their equilibrium values on the solvus lines.
- In the quasi-stationary-state regime ($t \geq 16$ h), the temporal exponents of the Al and Cr supersaturations in the matrix are -0.33 ± 0.04 and -0.34 ± 0.07 , respectively,

in approximate agreement with the multi-component coarsening model's [20,21] prediction of $-1/3$ (Fig. 11). Extrapolations from the γ -matrix far-field and γ' -precipitate core compositions to $t = \infty$ permit the equilibrium solvus line compositions to be determined (Table 2); 81.26 ± 0.18 Ni– 3.13 ± 0.08 Al– 15.61 ± 0.18 Cr at.% for the γ -matrix, and 76.5 ± 0.5 Ni– 16.7 ± 0.4 Al– 6.77 ± 0.30 Cr at.% for the γ' -precipitates.

- A linear $\langle R \rangle^3$ temporal dependence suggests that the coarsening mechanism is diffusion-limited. The experimental coarsening kinetics rate constant of $(8.8 \pm 3.3) \times 10^{-32} \text{ m}^3 \text{ s}^{-1}$ in the quasi-stationary state is found to be smaller than a model prediction [21] of $(0.56$ – $1.3) \times 10^{-30} \text{ m}^3 \text{ s}^{-1}$, which is attributed to diffusion occurring in both the γ - and γ' -phases and not solely in the γ -phase. The diffusivities in the γ' -phase are smaller than in the γ -phase.

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