Early stages of decomposition within the γ´ phase of a Ni-Al-Ti model alloy

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Abstract

A Ni-8.5Al-5.4Ti (at.%) model alloy was subjected to a two-step heat treatment resulting in the formation of γ´ precipitates in a γ matrix. The microstructural evolution was followed by transmission electron microscopy. Atom probe analyses at the nanometre scale showed the inhomogeneous distribution of Ni, Al and Ti in the γ´ precipitates. Ni-rich and Ni-depleted clusters were observed. The results are discussed with respect to the excess of Ni within the γ´ phase based on the conditions of heat treatment.

Keywords A. nickel aluminides, based on Ni3Al ; A. ternary alloy systems ; B. precipitates ; F. atom probe ; F. electron microscopy, transmission ; G. aero-engine components;

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1. Introduction

Ni-based superalloys are highly heat-resistant materials used for disks and blades in turbine engines. Appropriate heat treatment of such alloys leads to the formation of a two-phase microstructure which consists of coherent γ´ precipitates ($L1_2$-ordered) embedded in a γ solid solution matrix (A1-disordered). This two-phase microstructure is crucial for creep and fatigue resistance at high temperatures. The strength of Ni-based superalloys is mainly determined by the γ´ precipitates. However, under service conditions at elevated temperature, the cuboidal γ´ precipitates coarsen directionally and form rafts [1]. Although it has been controversially discussed in the past [2-4], it is generally well accepted that this morphological change of γ´ precipitates deteriorates creep resistance and thus reduces the lifetime of these materials [4-10].

Since the introduction of Ni-based superalloys in the 1940s there has been a remarkable development of this class of alloys, leading from polycrystalline to single crystal materials and shifting the maximum operating service temperature from 1173 K for first generation materials to about 1373 K for modern alloys [11]. However, the search for even further improved Ni-based alloys still continues due to their multiple advantages, e.g. creep rupture strength, despite advances in other materials, e.g. γ TiAl alloys [12].

Recently, a novel separation phenomenon in the γ´ phase has been reported, namely precipitation of γ particles within the γ´ precipitates during ageing after the homogenization heat treatment [13-15]. Such phase separation was not only observed in the ternary system Ni-Al-Ti [14, 15] which still remains one of the most important systems in superalloy metallurgy [16], but also in the ternary alloys Ni-Al-Fe [17], Ni-Si-Fe [17] and Ni-Al-Si [18]. Precipitation of γ within the γ´ phase and the successive division of cuboidal γ´ precipitates into smaller units result in a significant retardation of microstructure coarsening [15]. The evolution of the morphology of those γ precipitates within the γ´ phase of ternary Ni-8.5Al-

5.4Ti (at.%) alloy has been elaborated by transmission electron microscopy (TEM) [14] and transmission electron tomography imaging [15]. However, neither the mechanism of γ precipitation within γ´ precipitates is fully understood nor has the chemical composition of the newly formed γ particles been reported.

In the present study, the early stages of decomposition of γ´ precipitates in a Ni-8.5Al-5.4Ti (at.%) model alloy were investigated by three-dimensional atom probe (3D-AP). In addition, information on the evolution of the two-phase microstructure was obtained by transmission electron microscopy.

2. Experimental

A model alloy with a nominal composition of Ni-8.5Al-5.4Ti (at.%) with a purity of alloying elements of 4N, 5N and 4N, respectively, was produced in an argon atmosphere (2×10^{-3} Pa) using an induction furnace. After casting, the ingots were cut into plates (about. 10 x 20 x 1 mm) and the samples were heat treated at 1213 K for 45 minutes and subsequently aged at 1023 K for 6, 12 and 48 h in a quenching furnace under flowing argon. All heat treatments were followed by rapid removal from furnace and quenching in ice water. In order to observe the early stages of decomposition the pre-aging at temperatures above 1213 K was avoided in the present study which is different to the heat treatment used in Ref.'s [14, 15].

For transmission electron microscopy, discs of 3 mm diameter were punched out of the aged samples. Thin foils suitable for TEM were prepared by electrolytic jet polishing in a solution of 10% perchloric acid in 90% ethanol with 7 g thiourea at 253 K [19]. TEM measurements were carried out using a Philips CM30 microscope operating at 300 kV.

Square rods of 0.2 x 0.2 x 10 mm³ volume were cut out of the aged samples. Needle-shaped tips with a radius < 50 nm for 3D-AP analysis were prepared by electropolishing at

room temperature at a DC-voltage of about 15 V in two steps: 1) electropolishing in a solution of 15% perchloric acid in acetic acid; 2) micro-electropolishing using an electrolyte of 2% perchloric acid in butoxyethanol [19]. 3D-AP analyses were performed using a TAP, CAMECA [20], with instrument parameters of ultra-high vacuum $p < 10^{-6}$ Pa, a pulse-to-DC-voltage ratio of 0.2, a pulse repetition frequency of 1 kHz and a tip temperature of about 70 K.

3. Results and Discussion

The bright-field (BF) TEM micrograph of the Ni-Al-Ti alloy after heat treatment at 1213 K for 45 min shown in Fig. 1a exhibits a microstructure without visible γ´ precipitates. The corresponding selected area diffraction (SAED) pattern shows $L1_2$ superlattice reflections indicating long range order (LRO). The small dark regions indicated by arrows represent ordered areas. Typical microstructures of the alloy after the two-step heat treatments applied are shown in the BF-TEM micrographs displayed in Fig. 1b-c. A two-phase microstructure comprising a γ matrix and γ´precipitates is formed. The edges of the cuboidal γ´ precipitates are aligned along various <001> directions. The corresponding SAED patterns are shown in the insets of Fig. 1b-d. The electron diffraction pattern of the [001] zone axis exhibits superlattice reflections from γ´ precipitates. The γ´ phase is coherent with the fcc γ matrix. The strain contrast surrounding the γ´ particles is due to a lattice mismatch between γ matrix and γ´ phase. This behaviour is visible in BF-TEM images, whereas Dark Field (DF) imaging is not sensitive to strain contrast [21].

Fig. 2a exhibits a three-dimensional reconstruction of Ti atom positions in an analyzed volume of 8.7 x 8.7 x 105.0 nm^3 of the specimen aged at 1023 K for 48 h. Two regions are visible, a Ti-depleted and a Ti-enriched area, corresponding to the γ and γ´ phase, respectively. Ni and Al atoms have been omitted in this figure for reasons of clarity. The

average chemical compositions of γ and γ´phases for each ageing state are given in Table 1. The calculated volume fraction of the γ´ phase from 3D-AP data, $V\gamma'$, is also listed. Compositions and the volume fraction were found to have reached a constant state after 6 h of ageing.

Fig. 2b illustrates concentration depth profiles of all alloying elements evaluated along a cylinder of 3 nm diameter aligned along the centre of the reconstructed volume shown in Fig. 2a. The concentration values were calculated for cylinder slices of 0.5 nm thickness (i.e. a volume of ~ 3.5 nm^3) and each data point represents about 100 atoms. The concentration depth profiles of all elements in the γ´ phase indicate real fluctuations in concentration since they exceed the statistical error 2σ.

In order to quantify the inhomogeneous distribution of alloying elements within the γ´ phase, a statistical analysis, namely the cluster search module [22], was applied. The results of the analysis of clusters, composed of Ni, Al and Ti atoms, are shown in Fig. 3. Clusters containing more than 82 at.% Ni are shown within the γ´ phase in specimens aged for a) 6 h, b) 12 h and c) 48 h. In later stages, the ensemble of clusters appears to be interconnected, indicating the early stages of decomposition towards γ precipitation. The chemical compositions of Ni-enriched and Ni-depleted regions are listed in Table 2.

The nominal composition of the investigated alloy (C_{nom}), as well as the chemical compositions of γ and γ´ phases after heat treatment as measured by 3D-AP are plotted in a calculated ternary phase diagram, shown in Fig. 4a as an isothermal section at 1023 K [23]. The chemical compositions of γ´ phases after all ageing times investigated are all located well within the calculated γ´ phase existence area. The chemical compositions of Ni-enriched and Ni-depleted clusters within the γ´ phase are also shown. Obviously, the chemical

compositions of these Ni-rich and Ni-depleted clusters are located outside the γ´ phase existence area.

Recently published studies of the same alloy demonstrated the formation of γ precipitates within the γ´ phase [14, 15], whereas, in the present study, only clusters rich or depleted in Ni were found. This discrepancy can be explained by the different heat treatments of the alloys investigated. A two-step heat treatment with preceding homogenization was applied in Ref.'s 14 and 15, whereas in the present work, the two-step heat treatment alone was performed, without preceding homogenization. Initial homogenization of the Ni-Al-Ti alloy in Ref.'s 14 and 15 was performed at a temperature not explicitly specified but believed to be higher than 1213 K (in the γ single phase region) aiming at obtaining an A1 (fcc) solid solution. An already established γ/γ´ microstructure after homogenization at 1473 K for 1h was observed in the present study (not shown here). In contrast, the heat treatment at 1213 K for 45 min without preceding homogenization leads to the formation of a microstructure shown in Fig. 1a. In order to slow down the γ´ precipitation, the homogenization was omitted in this work. Therefore, the microstructure after ageing at 1213 K for 45 min was also different when compared with that in Ref.'s 14 and 15. Whereas in the present study only the very early stages of γ/γ´ separation are shown (Fig. 1a), the alloy in Ref.'s 14 and 15 contained cuboidal γ´precipitates, representing more advanced stages of ageing. Furthermore, this difference in heat treatment is the reason why in the present study only clusters were found within the γ´ phase and not γ precipitates as obtained in Ref.'s 14 and 15 after ageing at 1023 K.

A qualitative comparison with results of Tian et al. [24], shows that solubility of Ni in the γ´ phase could be responsible for phase separation. They reported the temperature dependence of the boundary between γ´ single-phase region and (γ+γ´) two-phase region of a Ni-Al-Ti alloy system as a function of (Al+Ti) and Ni content (see Fig. 4b). The Ti/Al ratio of their

alloy is 0.77 in contrast to 0.64 for the alloy of the present work. For example, the boundary shifts from about 78.8 at.% of Ni at 1213 K to 77.5 at.% at 1023 K. Thus, the solubility limit of Ni within the γ´ phase decreases as the temperature decreases. In Ref.'s 14 and 15 a higher amount of Ni is expected in the γ´ phase as a result of the homogenization treatment applied at a temperature above 1213 K. In those experiments, the first and second steps of aging were performed at 1213 K and 1023 K, respectively. Hence, at temperatures below 1213 K, the excess of Ni within the γ´phase will be reduced [24] in order to reach a local equilibrium state between γ and (γ+γ´) regions. This explanation also accounts for the decomposition of the γ´ phase towards Ni-enriched and Ni-depleted regions observed in the present study. The excess of Ni in the γ´phase was lower compared to that in Ref.'s 14 and 15 due to absence of the homogenization treatment (which would inherently lead to the precipitate formation of γ´ particles). Instead of γ particles within the γ´ phase, in this study, Ni-rich and Ni-depleted clusters were observed and their formation can be interpreted as the early stages of γ precipitation within the γ´ phase.

4. Conclusion

The combination of TEM and 3D-AP allows to follow the evolution of the two-phase microstructure (γ´precipitates and the γ matrix) after heat treatment at 1213 K for 45 min, quenching and subsequent ageing at 1023 K for 6 h, 12 h and 48 h.

Qualitative TEM analysis revealed $L1_2$ superlattice reflections for every state of ageing and showed formation of γ´ precipitates in the period from 6 h to 48 h of ageing. Although γ particles within the γ´ precipitates could not be observed, atom probe analyses on the nanometre scale showed that the distribution of Ni, Al and Ti in the γ´ precipitates is not homogeneous. A statistical analysis of 3D-AP data of the γ´ phases showed the existence of

Ni-rich and Ni-depleted regions. Decomposition within the γ´ phase was explained by the temperature-dependent solubility of Ni. Its amount in the γ´ phase reduces with decreasing temperature due to a local equilibrium state between γ and (γ+γ´) regions. The decomposition of the γ´ phase towards Ni-rich and Ni-depleted clusters can be seen as early stages of γ precipitation in the γ´ phase.

Figure captions

Figure 1. Bright-field TEM images of Ni-8.5Al-5.4Ti (at.%) alloy after a) heat treatment at 1213 K for 45 min, quenching and b-d) also subsequent ageing at 1023 K for b) 6 h, c) 12 h and d) 48 h. No cuboidal precipitates in a) but superlattice reflections indicate $L1_2$ structure. Precipitates with cuboidal morphology b-d) correspond to the ordered γ´ phase ($L1_2$ structure). The corresponding electron diffraction patterns of the [001] zone axis are shown in the inset.

Figure 2. a) Three-dimensional reconstruction of a region (8.7x8.7x105 nm³) of Ni-8.5Al-5.4Ti (at.%) alloy aged at 1023 K for 48 h containing a γ/γ´ interface. For the sake of clarity only the Ti atom positions are shown. b) Concentration depth profiles of the elements Ni, Al and Ti taken along a cylinder (not shown here) of 4 nm diameter oriented parallel to the long axis of the box shown in a) and approximately perpendicular to the γ/γ´ interface. The concentration values were determined in steps of 0.5 nm. The dashed line indicates the γ/γ´ interface.

Figure 3. Three-dimensional reconstruction of Ni-rich clusters (defined as > 82 at.% Ni) within γ´ precipitates of Ni-8.5Al-5.4Ti (at.%) alloy after heat treatment at 1213 K for 45 min, quenching and subsequent ageing at 1023 K for a) 6 h, b) 12 h and c) 48 h as evaluated using the cluster search module [22]. The inhomogeneous distribution of alloying elements within the γ´ phase is revealed. The length of the analyzed volumes is 25 nm, the edges are a) 7.8 x 7.8 nm², b) 8.6 x 8.6 nm² and c) 12 x 12 nm². The corresponding TEM images are also shown.

Figure 4. a) Ni-Al-Ti ternary phase diagram at 1023 K after Raghavan [23]. The nominal composition C_{nom} (X, green) of the alloy investigated and the composition of γ and γ´ phase after heat treatment at 1213 K for 45 min, quenching and subsequent ageing at 1023 K for 6 h (circles), 12 h (triangles) and 48 h (squares) of the present work are added. Ni-rich (blue symbols) and Ni-depleted (magenta symbols) decomposed regions in the γ´ phases are also given. b) Quasi-binary section of a Ni-(Al+Ti) phase diagram with X_{Ti}/X_{Al} = 0.77 after Tian et al. [24]. The boundary between γ´ single-phase and (γ+γ´) two-phase region of a Ni-Al-Ti alloy shows temperature dependent solubility of Ni in γ´ phase.

Table captions

Table 1. Compositions of γ and γ´ phases and the volume fraction $V_{\gamma'}$ of the γ´ phase in alloy Ni-8.5Al-5.4Ti (at.%) after heat treatment at 1213 K for 45 min, quenching and subsequent ageing at 1023 K. The error given is standard deviation 2σ.

Table 2. Compositions of Ni-rich and Ni-depleted regions within the γ´ phase after heat treatment at 1213 K for 45 min, quenching and subsequent ageing at 1023 K. Standard deviations 2σ are given.

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Table 1

	γ			γ´			
HT	Ni	Al	Ti	Ni	Al	Ti	$V_{\gamma'}$
6 h	90.47 ± 0.07	6.59 ± 0.06	2.95 ± 0.04	76.94 ± 0.43	13.36 ± 0.34	9.71 ± 0.30	32,28 ± 0,62
12 h	90.61 ± 0.49	6.27 ± 0.42	2.67 ± 0.27	74.77 ± 0.39	13.56 ± 0.31	11.67 ± 0.29	28,50 ± 0,33
48 h	90.57 ± 0.16	6.95 ± 0.14	2.47 ± 0.08	75.41 ± 0.10	14.16 ± 0.08	10.44 ± 0.07	29,50 ± 1,17

Table 2

	Ni > 82 at.%			Al > 18 at.%		
ST + HT	Ni	Al	Ti	Ni	Al	Ti
6 h	84.86 ± 1.14	9.18 ± 0.92	5.95 ± 0.75	71.68 ± 1.69	20.11 ± 1.07	8.21 ± 0.73
12 h	85.56 ± 1.84	7.02 ± 1.34	7.43 ± 1.38	69.39 ± 1.28	19.75 ± 1.10	10.85 ± 0.86
48 h	83.63 ± 1.16	9.12 ± 0.90	7.24 ± 0.81	68.32 ± 1.67	21.34 ± 1.47	10.33 ± 1.09

Figure(s)

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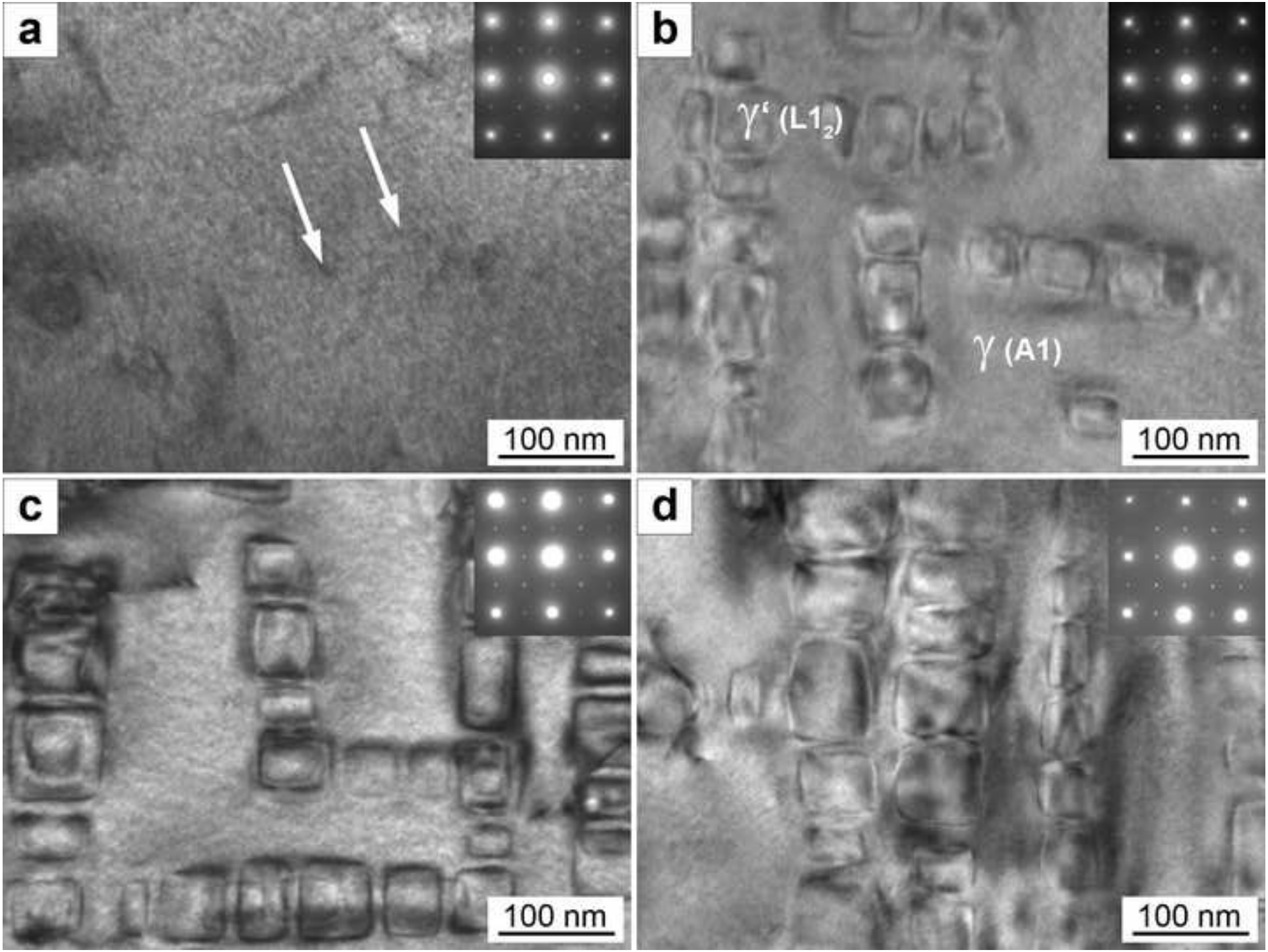

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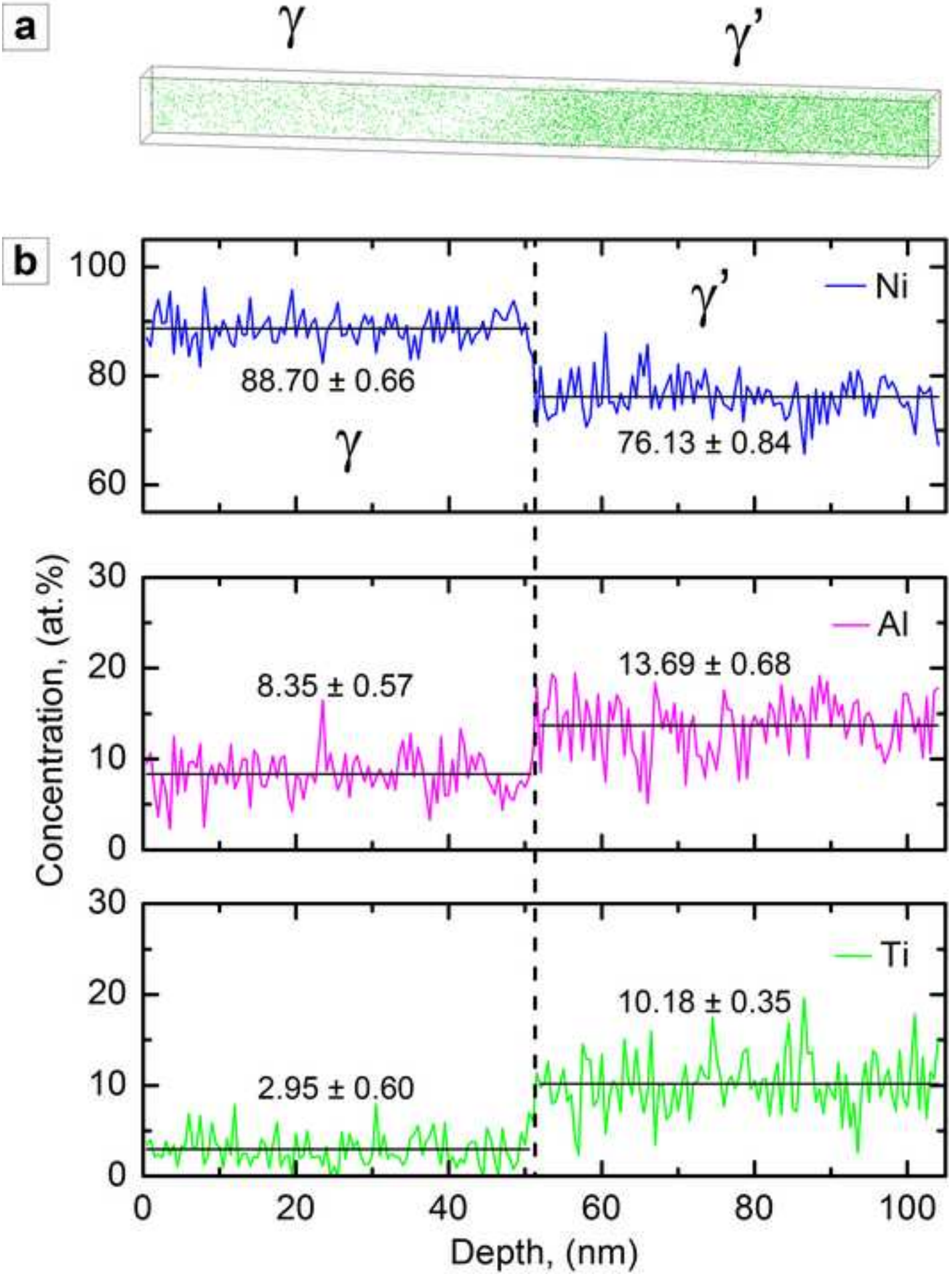

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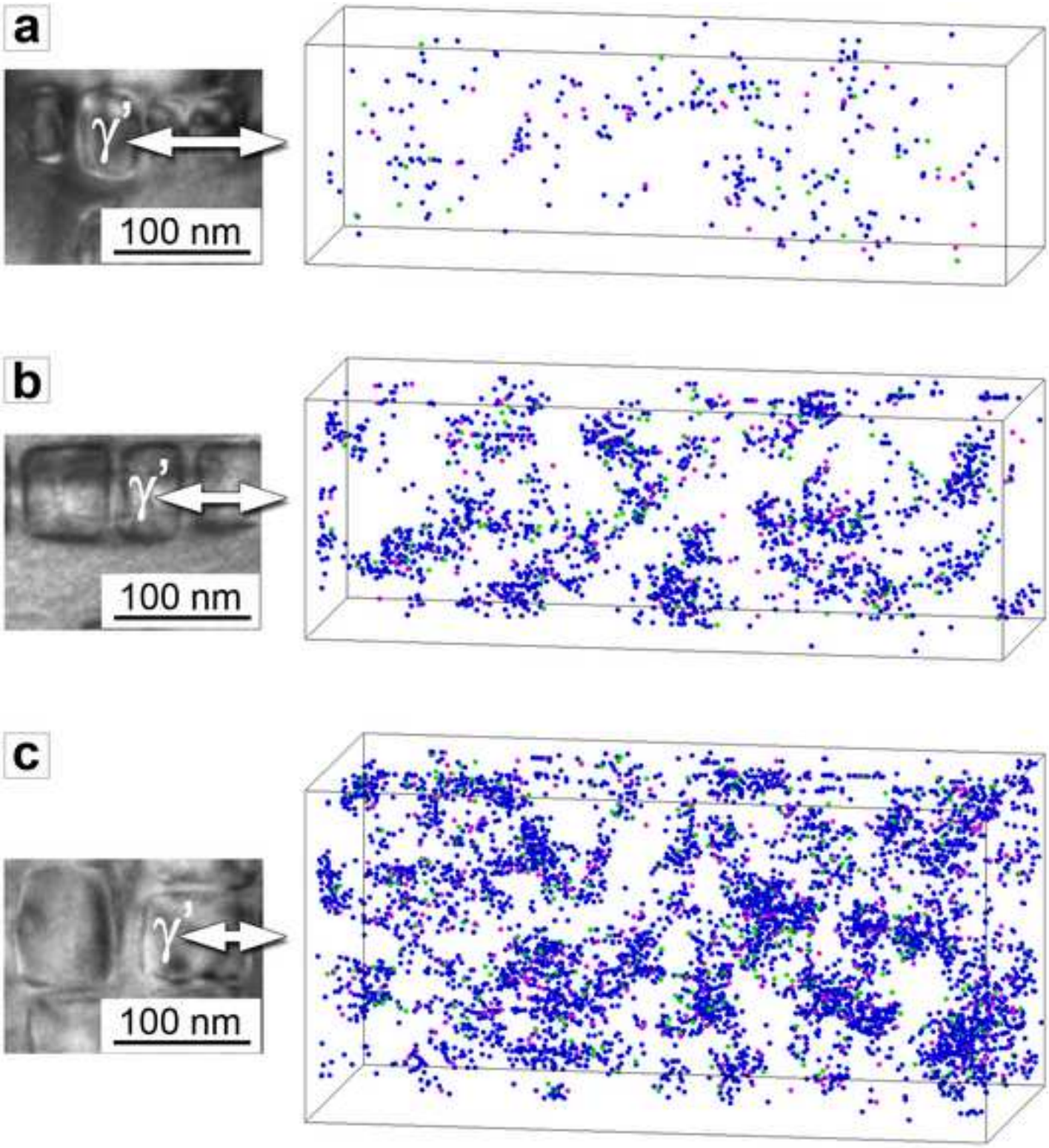

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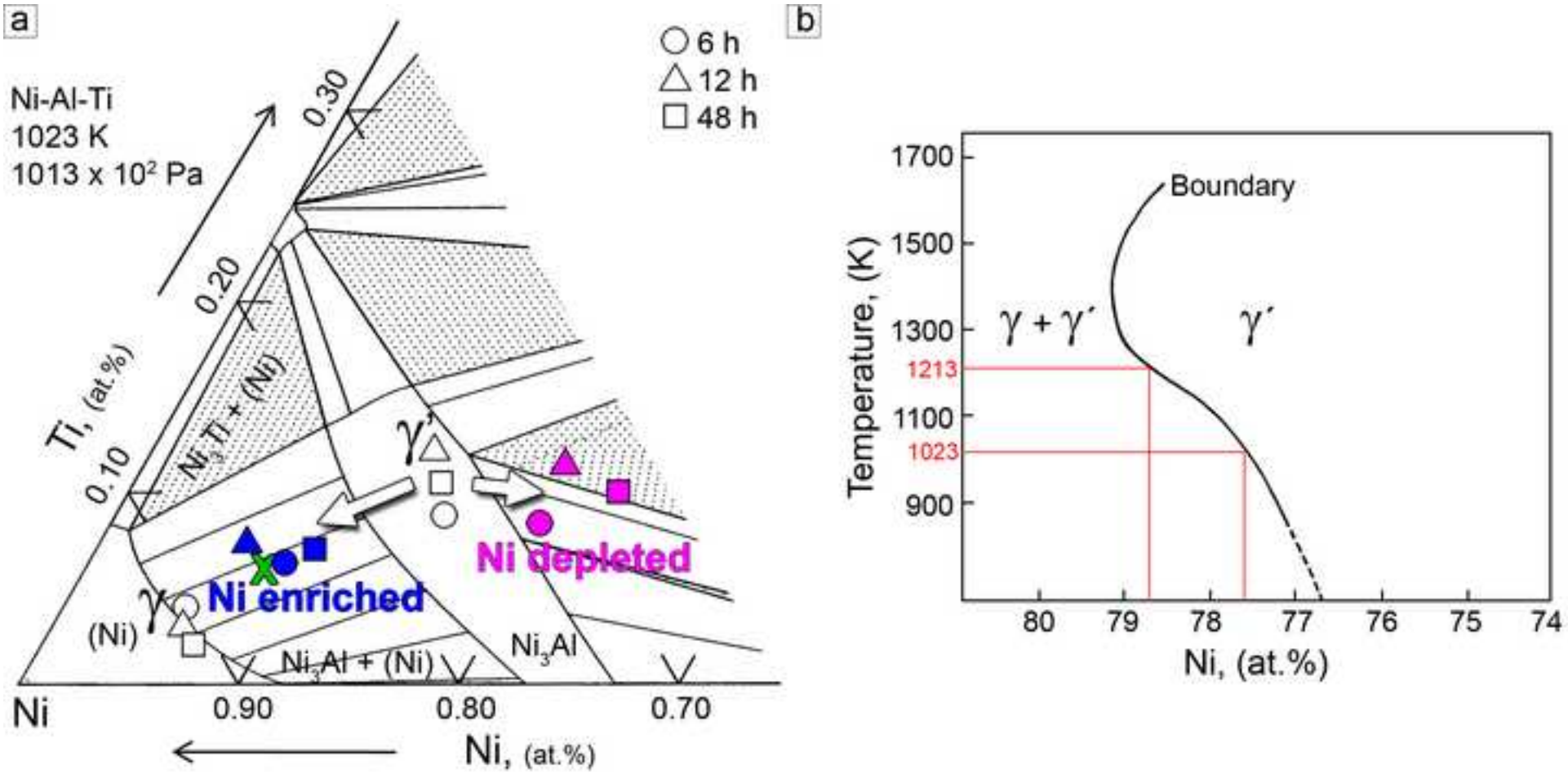

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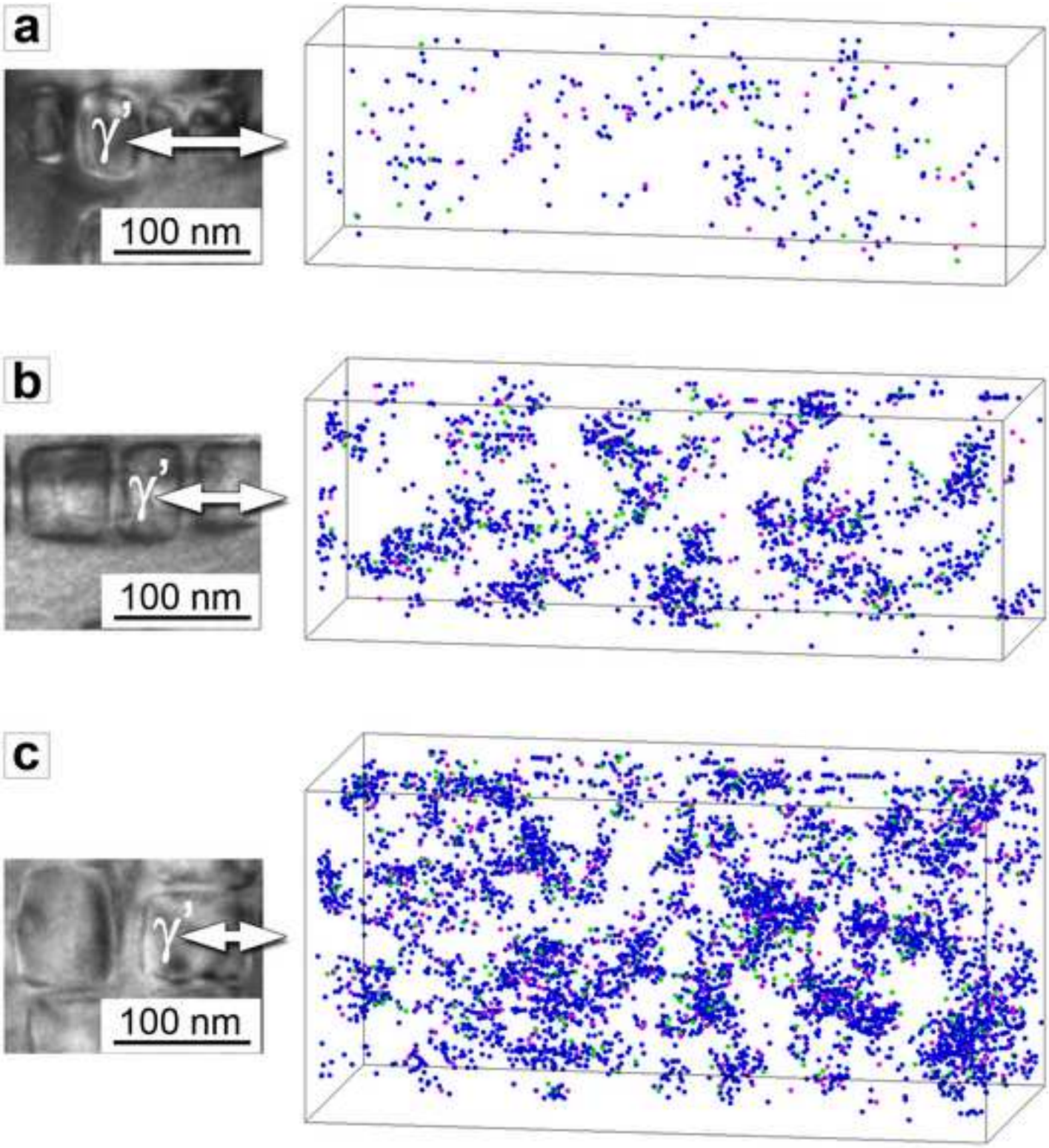

***Highlights**

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> Ni-Al-Ti model alloy to study decomposition of γ´ precipitates. > Ni supersaturation of γ´ precipitates leads to phase separation phenomenon after heat treatment at 1023 K. > Early stages of decomposition observed as clustering within γ´ precipitates.