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The influence of Cu addition on precipitation in Fe–Cr–Ni–Al–(Cu) model alloys

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ABSTRACT

Precipitation in Fe–Cr–Ni–Al–(Cu) model alloys was investigated after ageing for 0.25, 3, 10 and 100 h at 798 K. Characterization of nanoscale precipitates was performed using three-dimensional atom probe microscopy and transmission electron microscopy. The precipitates are found to be enriched in Ni and Al (Cu) and depleted in Fe and Cr. After 0.25 h of ageing the number density of precipitates is $\sim 8 \times 10^{24}\,m^{-3}$, their volume fraction is about 15.5% and they are near-spherical with an average diameter of about 2–3 nm. During further ageing the precipitates in the both alloys grow, but the coarsening behaviour is different for both alloys. The precipitates of the Cu-free alloy grow much faster compared with the Cu-containing alloy and their density decreases. Precipitates in Cu-free alloy change to plate shaped even after 10 h of ageing, whereas those of Cu-containing alloy remain spherical up to 10 h of ageing. The influence of Cu addition on precipitation in these model alloys is discussed with respect to the different coarsening mechanisms.

1. Introduction

Precipitation hardened (PH) stainless maraging steels have been developed for applications requiring a combination of good mechanical properties (yield stress and fracture toughness) and high corrosion resistance. The high strength of maraging steels is obtained by a solution heat treatment followed by an ageing treatment typically between 673 and 803 K. During ageing, precipitation of different intermetallic phases takes place. Maraging steels belong to the class of low-carbon steels. They contain a substantial amount of Cr, Ni and occasionally Co along with small additions of Al, Ti, Cu or Mn. Their composition is varied, depending on the application range envisaged. The variety of different precipitates that evolve depends both on the composition and heat treatment of the steel. Microstructural evolution, clustering, precipitation and hardening have been investigated in detail in many studies by atom probe analysis [1–8]. It was shown, e.g., that a small amount of Ti in maraging steel leads to the formation of several intermetallic phases, whereas in Ti-free alloy with a similar composition merely one intermetallic phase is created [9]. Addition of Cu to the maraging steel increases its hardness [4,10]. The investigation of structure, nucleation and growth of Cu precipitates was the subject of many studies. Ab-initio calculations of the mixing energies at 0 K predict that bcc Cu-precipitates in a bcc Fe matrix should be pure copper, but three-dimensional-atom probe (3D-AP) measurements show about 50 at% of Fe inside the Cu precipitates [11]. It was reported that in an Fe matrix Cu precipitates nucleate after extremely short ageing times due to the low solubility of Cu in ferrite and martensite below 773 K [4]. In a Fe–Cu–Ni alloy, nucleation of Cu takes place during quenching or room–temperature storage [12], whereas in an alloy with a larger amount of Ni and Cu, no Cu clusters were found in the lath martensite after water quenching [13]. There are also different findings of the morphological structure of Cu precipitates. For instance, some investigations show a core/shell structure of Cu-rich precipitates with a Cu core and a shell enriched in Ni and Al [14,15]. Others reported that Cu-rich precipitates contain some amount of Ni in the core after short ageing, but during further ageing Ni and Fe are rejected from these precipitates [16].

Because of the fast nucleation of small Cu precipitates found in the steel 1RK91 [4] and the investigations that show Cu precipitates combined with an intermetallic shell [14,15] or showing Ni-containing Cu precipitates [16], it was considered that the addition of Cu to a maraging steel should increase the number density and the volume fraction of the precipitates of its hardening phase.

Although nucleation and growth of Cu precipitates in steels have been investigated in several previous studies, there is a lack of understanding of the underlying process. To study the influence of a single element such as Cu on nucleation and growth of precipitates, simple alloys with a small number of elements are necessary. Therefore, two model alloys were cast for the present study: one is Cu-free, while the other contains 1.5 at% Cu.

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The concentration of the main elements (Fe, Cr, Ni and Al) corresponds to that of the commercial maraging steel *Corrax* [17]. This steel was chosen as reference for the model alloys because of prior investigations of this alloy by the authors [9,18] and because of their good mechanical properties at elevated temperatures and its good corrosion resistance as compared with other maraging steels.

In this paper we report on atom probe tomography measurements of the element distribution in Cu-free Fe–13Cr–8.7Ni–3.5Al (called "PH13-8H1") and in Cu-containing Fe–12.81Cr–8.55-Ni–3.4Al–1.5Cu (called "PH13-8Cu1.5") model alloys, both after solution heat treatment and ageing at 798 K for different times in order to elucidate the effect of Cu on nucleation and growth of precipitates. In addition, TEM was applied in order to investigate the structure of precipitates.

2. Experimental

The nominal composition of the investigated Fe–Cr–Ni–Al–(Cu) model alloys is given in Table 1. The ingots from materials of different high purities—Ni, Al (99.999%), Fe, Cu (99.99%) and Cr (99.2%)—were cast in an induction furnace under argon atmosphere (2×10^{-5} mbar and $<10^{-15}$ ppm O_2). Cold rolling of the ingots was performed up to 80% reduction in thickness in order to reduce their porosity. The alloys were then solution heat treated at 1123 K for 0.5 h in an argon atmosphere and subsequently cooled to room temperature by Ar gas flow. After this, the samples were aged at 798 K for 0.25, 3, 10 and 100 h.

Platelets of $1\times1\,mm^2$ size were mechanically ground to a thickness of about 10 μm, mounted onto a 3 mm titanium ring appropriate for being used in TEM and then ion beam milled at room temperature with Ar^+ to achieve electron transparency. The conventional TEM investigations were performed using a Philips CM30 microscope operated at 300 kV.

Three-dimensional atom probe analyses were performed with a CAMECA instrument [19]. In order to prepare tips for 3D-AP investigations, small rods with a cross section of $0.2\times0.2\,mm^2$ were cut. Sharp tips were prepared using standard techniques by electrolytical polishing as described in Ref. [7]. Samples after solution heat treatment as well as after ageing at 798 K were investigated. All atom probe analyses were performed at a temperature of 60 K with a pulse fraction ratio (pulse voltage to the standing tip voltage) of 0.2 and with a pulse repetition rate of 1 kHz in ultrahigh vacuum of 1×10^{-8} Pa.

Table 1
Nominal composition of the model alloys investigated (at%).

Model alloys	Fe	Cr	Ni	Al	Cu
PH13-8H1	74.86	13.00	8.68	3.45	–
PH13-8Cu1.5	73.74	12.81	8.55	3.40	1.50

3. Results

3.1. Solution heat treatment

Alloys PH13-8H1 and PH13-8Cu1.5 were investigated by 3D-AP after solution heat treatment. No clusters or precipitates are visible after this heat treatment. Whether the alloying elements are homogeneously distributed within the analyzed volume or not was investigated by wavelength-dependent filtering (WDF) analysis [20] and by using a cluster search algorithm [21]. The results (not shown here) of both statistical evaluation techniques reveal that these alloys do not contain concentration fluctuations or clusters of alloying elements, hence, the alloys appear to be homogeneous after solution heat treatment.

3.2. Ageing for 0.25 h

Fig. 1 shows a three-dimensional reconstruction of the location of Ni and Al atoms within an analyzed volume $7\times7\times50\,nm^3$ of the alloy PH13-8H1. The reconstructed volume contains regions enriched in Ni and Al and depleted of Cr and Fe. These regions are nearly spherical with an average diameter of 2–3 nm. Their number density is about $8.5\pm2.0\times10^{24}\,m^{-3}$ and their volume fraction is $15.5\pm3.3\%$ as measured by 3D-AP. Al and Ni were chosen to be displayed in the figures as representative elements due to their precipitation during ageing.

Agglomerations of Ni, Al and Cu atoms are also observed in the alloy PH13-8Cu1.5 after short ageing. Fig. 2 shows three-dimensional reconstructions of Ni, Al and Cu atom positions within the $11\times11\times34\,nm^3$ analyzed volume. The shape of the precipitates is also nearly spherical with an average diameter of 2–3 nm. The number density of the precipitates is $6.3\pm1.2\times10^{24}\,m^{-3}$ and the volume fraction of the precipitates $15.7\pm3.1\%$. Shape, size and the number density of precipitates are similar for Cu-free and Cu-containing alloy.

The chemical compositions of the precipitates in the alloys PH13-8H1 und PH13-8Cu1.5 are given in Table 2. Besides the enrichment of Ni, Al and Cu in the precipitates, the amount of Fe is high, up to 61 at% for Cu-free and ~42 at% for Cu-containing alloy.

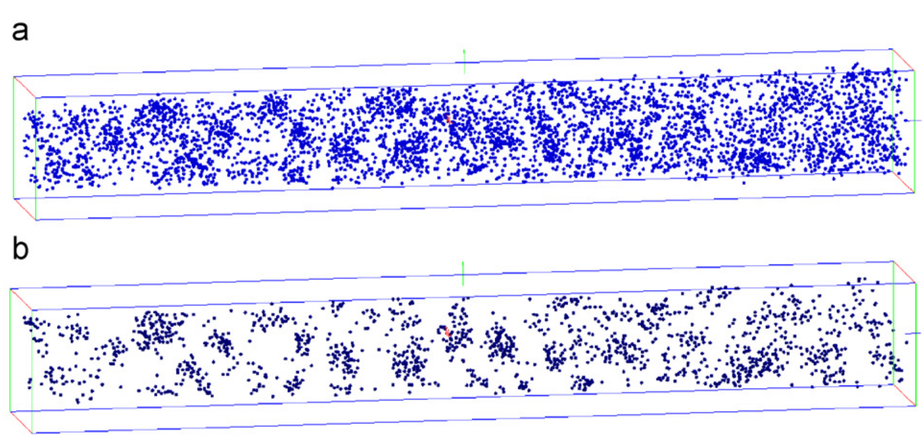

Fig. 1. 3D reconstruction of the atom positions of (a) Ni and (b) Al after 0.25 h at 798 K of the Cu-free alloy. Small precipitates enriched in Ni and Al with a high number density are obtained in an investigated volume of $7\times7\times50\,nm^3$.