Precipitate modification in PH13-8 Mo type maraging steel

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Abstract

The evolution of precipitates in PH13-8 Mo type stainless maraging steel alloyed with Cu was investigated during aging at 525 °C. Atom probe tomography was used to follow the evolution of precipitates with respect to type and chemical composition. It was found that Cu modifies the precipitation sequence in such alloys. Instead of $Ni_3(Ti,Al)$ and G-phase the formation of NiAl and G-phase occurred. The modification of the precipitation sequence is due to the incorporation of Cu in NiAl precipitates. However, both types of precipitates develop out of an undefined precursor phase, in contrast to other Cu-alloyed PH13-8 Mo maraging steel grades.
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1. Introduction

A number of studies have been carried out on the microstructural aspects of PH13-8Mo grade steels. In these studies the main focus has been on the evolution of precipitation in the different steel grades [1–10]. It has been shown that PH13-8Mo maraging steels, containing Ni and Al as age hardeners, are strengthened by the formation of an ordered β′-NiAl phase with a B2 (CsCl) superlattice structure [11–14]. This structure consists of two interpenetrating primitive cubic cells, where the Al atoms occupy the cube corners of the first sublattice and the Ni atoms occupy the cube corners of the second sublattice. The lattice constant of the stoichiometric composition is 0.2887 nm [15], which is of the same order of magnitude as the lattice constant for ferrite (0.28664 nm) [16]. Due to this fact, the NiAl precipitates are coherent with the matrix and remain coherent after long

aging times [1,12]. Precipitation takes place immediately after heating the material to the aging temperature [17]. However, the composition of the precipitates, even after longer aging times, is far from the stoichiometric NiAl phase, since the precipitates contain a significant amount of Fe [13,18]. However, it is generally thought that their formation proceeds via solute-rich clusters within the martensitic matrix. Coherent NiAl precipitates are formed out of these nuclei and are uniformly distributed within the matrix [11].

In contrast, it has been reported that strengthening in steel grades additionally alloyed with Ti is caused by the precipitation of η-phase ($Ni_3(Ti,Al)$) [9,19–21]. The η-phase exhibits a hexagonal lattice with $a = 0.255$ nm and $c = 0.42$ nm [22]. The orientation relationship between the η-phase and the martensitic matrix was found to be $(0\ 1\ 1)_M \| (0\ 0\ 0\ 1)_\eta$; $[1–11]_M \| [11–20]_\eta$ [21,23–25]. In the literature some debate exists on the mechanism of formation of the η-phase. Most of the studies found propose heterogeneous nucleation on dislocations, with subsequent growth taking place via pipe diffusion [26–28]. Others have advanced the theory that first coherent zones form on dislocations in the martensitic matrix, acting as nucleation sites for the η-phase [21,26]. There is also a discrepancy

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regarding the dominant strengthening mechanism in this kind of maraging steel. While the majority of studies attribute strengthening to the formation of Ni_3Ti, others have proposed an additional contribution from some B2-type ordering of Fe and Ni atoms in the matrix [21].

A further type of precipitate phase, termed the G-phase, was found by Gemperle et al. [29] in Ti-containing maraging steels alloyed with Si. The G-phase exhibits the chemical composition $Ti_6Si_7Ni_{16}$ and precipitates primarily on grain boundaries. Depending on the chemical composition of the alloy, the G-phase ($Ti_6Si_7Ni_{16}$) and the η-phase (Ni_3Ti) can precipitate either simultaneously or separately [29]. The shape of the η-phase is thought to be rod-like, while the G-phase shows a spherical morphology. Later studies by Schober et al. [14] revealed that both the spherical G-phase and the rod-shaped η-phase are formed independently from an undefined precursor phase, which is responsible for strengthening up to peak hardness. Recently atom probe tomography (APT) was used to follow the precipitation sequence in a Si-free Fe–Cr–Ni–Al–Ti stainless steel during aging at 525 °C [18]. In that work, instead of splitting into G-phase ($Ti_6Si_7Ni_{16}$) and η-phase (Ni_3Ti), formation of spherical NiAl particles and elongated $Ni_3(Ti,Al)$ particles from an undefined precursor phase was found in the early stages.

Another age hardener in maraging steels is copper. It is used in PH 15-5 and PH 17-4 alloys as a precipitating hardening element, but also in complex alloy systems, such as the commercial maraging steels 1RK91 and C455, as nucleation sites for the precipitation of the strengthening phase [30–32].

In the case of 1RK91 the precipitation sequence starts with the formation of a Ni/Ti/Al-rich phase nucleating on Cu-rich clusters [32–35]. During further aging $Ni_3(Ti,Al)$ precipitates develop adjacent to Cu-rich precipitates. In C455, which contains less Al and no Mo, clusters of Cu, Ti and Ni form in the early stages, which are thought to be a precursor phase of η-Ni_3Ti [33,35]. Extended aging treatment then leads to separation of the Ni-rich (η-Ni_3Ti) and Cu-rich precipitates. The effect of Cu on precipitation evolution in PH13-8Mo maraging steel, which exhibits NiAl and η-phase precipitates, was recently investigated by Schnitzer et al. [17]. This study revealed the formation of NiAl out of a Cu-containing precursor phase and nucleation of the η-phase on independent Cu clusters.

To sum up, an almost comprehensive picture of precipitation behavior in PH13-8Mo type maraging steels exists. Only the influence of Cu on the formation of G-phase is missing.

The aim of the present study was therefore to investigate the effect of Cu on the recently observed splitting phenomenon in Fe–Cr–Ni–Al–Ti–Si maraging steels. The precipitates are examined using an advanced three-dimensional (3-D) atom probe in order to follow their compositional changes during aging and to determine the distribution of alloying elements in the precipitates.

2. Experimental

The maraging steel investigated is a model alloy of type Fe–Cr–Ni–Al–Ti–Si–Cu. Its chemical composition is listed in Table 1. It should be noted that all compositions presented in this paper are given in at.% and the elements which are not relevant for age hardening in this alloy, i.e. Mo and Cr, are not taken into account in the description of the results and the discussion. The material was produced by melting a pellet with a diameter of approximately 40 mm and a height of 5 mm in an induction furnace under an argon atmosphere. Afterwards the material was homogenized at 1148 °C for 48 h. Subsequently the material was subjected to solution annealing at 1000 °C for 1.5 h, followed by air cooling. Aging was performed at 525 °C for of 0.25, 3, and 10 h in a Bähr Dil 805A quenching dilatometer. Heating to the aging temperature and cooling to room temperature was conducted within 5 s. These parameters are equal to the ones used in Leitner et al. [18]. For APT small rods with a cross-section of 0.3×0.3 mm were cut from the dilatometer samples and then etched to sharp needles by a standard two-step electropolishing technique [36]. APT was performed in a LEAP™ 3000 X HR atom probe at base temperatures of 20 and 60 K. APT was carried out in both voltage pulse and laser pulse mode. The latter was used for the brittle condition, as the evaporation is gentler, so the risk of specimen fracture decreases. Pre-investigations revealed a laser energy and repetition rate of 0.2 nJ and 200 kHz, respectively, as suitable to obtain overall compositions comparable with the nominal composition in such alloys [17]. It should be noted that in the present work the overall composition in all measured states matches the nominal one well apart from some small deviations, which might be attributed to element segregation because of the as-cast state of the alloy. In the case of voltage runs a pulse fraction of 20% was used. Data reconstruction and statistical evaluation was conducted using the software package IVAS™ 3.4.3 from Imago Scientific Instruments (Madison, WI). Frequency distribution analysis [37,38] was performed to examine the distribution of elements in the analyzed volume. Clusters were detected by applying a cluster search algorithm based on the maximum separation method [39]. The separation distance (d_{max}), the surround distance (L), the erosion distance (d_{ero}) and the minimum number of atoms (N_{min}) were determined based on a method described elsewhere [40]. Clearly visible enriched regions in an analyzed volume were defined by isoconcentration surfaces [41]. Based on these isosurfaces, proximity histograms [42,43] were calculated to obtain information on the chemical composition of these regions.

Table 1
Chemical composition of the investigated maraging steel (at.%).

Fe	Cr	Ni	Si	Ti	Al	Mo	Cu	Mn	C
Balance	113.22	9.26	1.7	0.6	2.26	0.58	0.44	0.06	0.09