Precipitation Characteristics of Cu-rich and NiAl Phases in the Two-phase Region of Precipitation-Strengthened Steel (Postprint)

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Abstract

Precipitation-hardening steel was solution-treated at 900°C for 2 h, quenched, and aged at 500°C for 1 h. The precipitation characteristics of strengthening phases in the retained austenite and martensite two-phase region were investigated using atom probe tomography. The results show that no precipitates formed in the retained austenite, while precipitation occurred in the martensite and at the martensite/retained austenite interfaces. A precipitation-depleted zone existed in the martensite near the interface. The equivalent radius and spacing of precipitates at the interface were both larger than those in the martensite. The contents of Cu, Ni, and Al elements in the Cu-rich and NiAl phases at the interface were higher than those in the martensite, and the phase separation tendency of the Cu-rich and NiAl phases at the interface was greater than that in the martensite. This is because numerous defects at the interface promoted the growth of strengthening phases, placing the precipitates at the interface and in the martensite at different stages of growth.

Full Text

Preamble

Precipitation Characterization of NiAl and Cu-Rich Phases in Dual-Phase Region of Precipitation Strengthening Steel

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Abstract

Precipitation strengthening plays an important role in improving the mechanical properties of steels, with NiAl and Cu-rich phases being two common types of precipitates. This work aims to reveal the precipitation characteristics of these two phases in martensite and retained austenite in precipitation strengthening steel by atom probe tomography (APT). Hot-rolled samples were aged at 500 °C for 1 h after solution treatment at 900 °C for 2 h, followed by microstructure analysis. The results show that NiAl and Cu-rich phases form in the martensite phase as well as at martensite/austenite phase boundaries, while no precipitate develops in retained austenite. A precipitation-free zone was observed near the phase boundaries in martensite. The equivalent radius, spacing, and concentration of strengthening phases at the phase boundary are larger than those inside martensite. In addition, the NiAl phase tends to separate from the Cu-rich phase, and this separation tendency becomes stronger at phase boundaries than in martensite. The growth of NiAl and Cu-rich phases at the phase boundary differs from that within martensite, which should be induced by the defect density difference between them.

Key Words retained austenite, martensite, phase boundary, strengthening phase, atom probe tomography

Precipitation strengthening is one of the most important strengthening mechanisms in steel materials, with Cu-rich and NiAl phases being two common precipitate types in precipitation-strengthening steels. During aging of Cu-containing precipitation-strengthened martensitic steels, a metastable bcc-structured Cu-rich phase first forms coherently with the matrix, which gradually grows and eventually transforms into a stable fcc structure with extended aging time [1-7]. In Cu-containing precipitation-strengthened austenitic steels, the Cu-rich phase directly forms as a stable fcc-structured -Cu during aging [8-10]. In precipitation-strengthened martensitic steels containing Ni and Al, coherent NiAl phases with B2 structure precipitate after aging above 400 °C [11-14].

In martensitic steels containing Ni, Al, and Cu simultaneously, both Cu-rich and NiAl phases precipitate after aging treatment. Zhang et al. [15] used atom probe tomography (APT) to investigate precipitation characteristics in a steel containing Ni, Al, and Cu after aging at 500 °C for 10 h, observing that Cu-rich and NiAl phases precipitated in adjacent locations. Isheim et al. [6] and Vaynman et al. [16] also employed APT to study Cu-rich and NiAl phases in NUCu series martensitic steels after aging at 500 °C for different times, finding that a core-shell structure formed with Cu-rich phase as the core and $Ni_{0\cdot5}(Al_{0\cdot5}$ Mn) phase in the outer layer as aging time increased.

Xiang et al. [17] used scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to investigate Cu-rich phase precipitation in ferrite-austenite duplex stainless steel, finding that during aging at 540-580 °C, Cu-rich phases formed only in ferrite and at ferrite/austenite interfaces. Due to the small size of Cu-rich phases (only a few nanometers) and the limited resolution of SEM and TEM, no further investigation of the characteristics of Cu-rich phases at these two locations was conducted.

The aforementioned studies investigated Cu-rich phase precipitation in martensite (or ferrite), NiAl phase precipitation in martensite (or ferrite), simultaneous presence of Cu-rich and NiAl phases in martensite, and Cu-rich phase precipitation in ferrite-austenite duplex steels. However, they did not address the precipitation behavior of Cu-rich and NiAl phases when martensite (or ferrite) and austenite coexist. This work selects a precipitation-strengthening steel containing Ni, Al, and Cu, and uses APT to investigate the precipitation characteristics of Cu-rich and NiAl phases in the dual-phase region of martensite and retained austenite.

Experimental

The chemical composition of the experimental precipitation-strengthening steel is shown in . The steel was solution-treated at 900 °C for 2 h, water-quenched, and then aged at 500 °C for 1 h. A LEAP3000TM HR atom probe was used to investigate the precipitation characteristics of strengthening phases in retained austenite, within martensite, and at martensite/retained austenite interfaces. Atom probe specimens were cut by spark machining into square rods with cross-sectional dimensions of 0.5 mm × 0.5 mm, and then prepared by a two-step electropolishing method [18]. During data acquisition, the specimen temperature was cooled to 50 K, the pulse voltage frequency was 200 kHz, and the pulse fraction was 15%. The obtained data were analyzed using IVAS 3.6.2 software. The equivalent radius (Rp) of strengthening phases was calculated using the maximum separation envelope method (MSEM) [18], with separation distance (SP) and minimum number (MN) parameters set to 0.3 nm and 60, respectively.

Chemical compositions of the precipitation-hardening steel (mass fraction/% and atomic fraction/%)

2. Experimental Results and Discussion

[Figure 1: see original paper] shows three-dimensional APT maps of various alloying element distributions. Carbon atoms are distributed in two distinct regions within the analyzed volume: a C-rich region and a C-depleted region (Fig. 1a). To accurately identify these regions, one-dimensional concentration profiles of C were constructed along the arrow direction in Fig. 1a, as shown in [Figure 2: see original paper]a. The average C content in the C-rich region is (2.3 ± 0.6) at%, which exceeds the average composition of 0.69 at% and thus corresponds to retained austenite (RA) with a thickness of approximately 16 nm. The C content in the C-depleted region is (0.4 ± 0.3) at%, which is lower than the average C content and corresponds to martensite (M).

Manganese is enriched at the martensite/retained austenite (M/RA) interface, as shown in Fig. 1b. To quantify this enrichment, a one-dimensional concentration profile was constructed along the arrow direction in Fig. 1b, as shown in Fig. 2b. The peak Mn concentration reaches (5.7 ± 0.6) at%, while the Mn contents in martensite and retained austenite are (1.0 ± 0.8) at% and (2.3 ± 0.4) at%, respectively. Dmitrieva et al. [19] also observed lamellar Mn segregation at martensite/austenite interfaces in high-Mn TRIP steel aged at 450 °C for 48 h. This occurs because, although the alloy element concentration is higher in retained austenite and lower in martensite, Mn atoms from martensite diffuse rapidly to the interface under a chemical potential gradient. The closely-packed austenite cannot absorb all these Mn atoms in a short time, resulting in Mn enrichment at the interface [19], which reduces the total system energy.

Figures 1c-e reveal that Ni, Al, and Cu all form spherical clusters in martensite and at the M/RA interface, and these clusters occur at the same locations, indicating the formation of NiAl and Cu-rich phases. Similar phenomena were reported in references [11,12,20]. No elemental clustering was observed in retained austenite, consistent with observations in references [17,19], because Ni, Al, and Cu have relatively high solubility in retained austenite and do not reach supersaturation. A lamellar region near the M/RA interface in martensite shows no precipitation of either NiAl or Cu-rich phases. This precipitate-free zone (PFZ) forms because precipitation at the interface consumes surrounding solute atoms, reducing the Ni, Al, and Cu contents in nearby martensite below the supersaturation level required for nucleation.

To investigate precipitation characteristics at the M/RA interface and within martensite, the equivalent radius and average spacing of strengthening phases were calculated. The results show that precipitates at the M/RA interface have a larger radius (1.8 ± 0.6 nm) than those in martensite (1.4 ± 0.4 nm). This is attributed to the high density of defects at the interface, which facilitates nucleation of strengthening phases and enhances diffusion of alloying elements, accelerating solute atom accumulation on nuclei. Consequently, the growth rate of precipitates at the interface exceeds that in martensite. The average spacing of precipitates at the interface (6.2 nm) is also larger than in martensite (1.6 nm). This occurs because the solid solubility of alloying elements is higher on the austenite side of the interface, resulting in lower supersaturation and fewer nucleation sites. Additionally, the faster growth rate of precipitates at the interface contributes to the larger spacing.

[Figure 3: see original paper]a shows three-dimensional distributions of the two strengthening phases obtained using iso-concentration surfaces, with green particles representing Cu iso-concentration surfaces at 5 at% and red particles representing Ni+Al iso-concentration surfaces at 20 at%. The precipitation characteristics of NiAl and Cu-rich phases differ in the dual-phase region: Cu-rich phases form on the side adjacent to retained austenite, while NiAl phases form on the side adjacent to martensite. To further investigate precipitation features at the interface and within martensite, specific precipitates were selected for analysis: ppt1 and ppt2 at the interface, and ppt3 and ppt4 in martensite (indicated by arrows in Fig. 3a). Figures 3b-e show enlarged views of precipitates ppt1-ppt4.

The compositions of NiAl and Cu-rich phases in these four precipitates are listed in . In both the interface and martensite regions, the Ni:(Al+Mn) ratio in NiAl phases is approximately 1:1, indicating that Mn substitutes for Al atoms to form Ni(Al,Mn) phases. The contents of Cu, Ni, and Al in precipitates at the interface are higher than those in martensite, particularly the Cu content in Cu-rich phases at the interface, which is significantly higher than in martensite. This is because the high defect density at the interface accelerates precipitation and growth, leading to greater enrichment of Cu, Ni, and Al in interfacial precipitates.

One-dimensional concentration profiles along the arrow directions in Figs. 3b-e are shown in [Figure 4: see original paper]. In interfacial precipitates ppt1 (Fig. 4a) and ppt2 (Fig. 4b), the concentration peaks of Cu-rich and NiAl phases are separated by approximately 1.5 nm, indicating a separation trend between the two phases. This phenomenon is similar to that observed in the same steel aged at 500 °C for 4 h [21]. In contrast, for precipitates ppt3 (Fig. 4c) and ppt4 (Fig. 4d) in the martensite matrix, the concentration peaks of NiAl and Cu-rich phases essentially coincide, indicating that the two phases have not yet separated.

During early aging stages, Cu-rich phases formed in the martensite matrix have a bcc structure with lattice constants close to those of the B2-structured NiAl phase [22,23]. Therefore, regardless of which phase nucleates first, its coherent interface with the matrix provides nucleation sites and energy for the other phase to precipitate nearby, resulting in the concurrent formation of NiAl and Cu-rich phases. With extended aging, Cu-rich phases in martensite undergo a structural transformation from bcc Cu → 9R Cu → 3R Cu → fcc -Cu [24], eventually forming stable fcc-structured -Cu, while NiAl phases retain their B2 structure. This structural difference inevitably leads to separation between the phases. The high defect density at the interface accelerates this structural transformation, and because one side of the interface is fcc-structured retained austenite, Cu-rich phases at the interface more readily transform to fcc-structured -Cu or even form -Cu directly. Thompson et al. [25,26] and Ricks et al. [27] observed direct formation of fcc-structured -Cu at austenite/ferrite interfaces during continuous cooling of HSLA steels. The -Cu tends to grow toward the fcc-structured retained austenite side, while the B2-structured NiAl phase, having smaller lattice mismatch with the martensite matrix, naturally grows closer to the martensite side, resulting in separation of NiAl and Cu-rich phases at the interface.

Although the experimental sample was aged at 500 °C for only 1 h, the strengthening phases at the interface and in martensite are at different growth stages. The growth rate of NiAl and Cu-rich phases at the interface exceeds that in martensite. Consequently, Cu-rich phases at the interface have already transformed to -Cu, while those in martensite remain bcc-structured. Additionally, the enrichment levels of Cu, Ni, and Al are higher at the interface, and NiAl and Cu-rich phases show a separation trend at the interface.

[Figure 4: see original paper] One-dimensional concentration profiles along the arrows marked in Figs. 3b-e: (a) ppt1, (b) ppt2, (c) ppt3, (d) ppt4

3. Conclusions

1. In precipitation-strengthening steel containing Ni, Al, and Cu, after quenching and aging at 500 °C for 1 h, APT observations reveal coexistence of martensite and retained austenite. No precipitates form in retained austenite, while strengthening phases precipitate both at martensite/retained austenite interfaces and within martensite. A precipitate-free zone exists in martensite near the interface.
2. Defects at the martensite/retained austenite interface promote solute atom diffusion and accumulation, accelerating precipitate growth. Consequently, the size and spacing of precipitates at the interface are larger than those in martensite, and the concentrations of precipitate-forming elements are higher at the interface.
3. The separation between Cu-rich and NiAl phases is more pronounced at the phase interface than in martensite. This is because the rapid growth at the interface facilitates transformation of Cu-rich phases to stable fcc-structured -Cu on the fcc retained austenite side, while the bcc-structured NiAl phase tends to grow on the martensite side.

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