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The relation between aging temperature, microstructure evolution and hardening of Custom 465® stainless steel

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ABSTRACT

The microstructure and hardness of Custom 465® precipitation hardened stainless steel were characterized following 4 hours aging at temperatures ranging from 482 °C to 648 °C. Dilatometry measurements and thermodynamic calculations were used to understand the mechanism of martensite-to-austenite reversion. Three major stages of aging were observed. The first stage is the peak hardening at aging temperatures of 480–510 °C, where both η-Ni_3Ti precipitation and austenite reversion begin independently of each other. The second stage is the initial stage of overaging observed above 538 °C as reduction in hardness is due to a slight increase in both the precipitate dimensions and the reverted austenite volume fraction. The third, progressive overaging stage occurs above 593 °C in which a dramatic hardness decrease is caused by a significant increase in both precipitate dimensions and reverted austenite volume fraction. Transmission Kikuchi diffraction orientation mapping revealed that globular austenite randomly nucleates at martensite grain boundaries, while acicular austenite nucleates along martensite lath boundaries. Thermodynamic calculations indicated that the dissolution of η-Ni_3Ti precipitates does not govern the austenite reversion, although both phases are in competition for Ni. While the thermodynamic calculation predicts increase in the fraction of austenite with increase in aging temperature, the fraction of austenite found at room temperature in aged samples does not vary when the aging temperature, in which austenite reversion occurs, is increased above 593 °C. This is explained by the change in composition of the austenite as a function of aging temperature.

1. Introduction

Custom 465® precipitation hardened (PH) stainless steel is a martensitic age-hardened alloy characterized by a combination of high strength, high fracture toughness and good resistance to general corrosion and stress corrosion cracking (SCC), compared with other high-strength PH stainless steels such as Custom 455 and Carpenter 13–8 [1]. Hardening of Custom 465® upon aging is attributed to the formation of the intermetallic hexagonal η-Ni_3Ti phase in the form of rod-shaped nano-precipitates [2]. The formation of rod-shaped η-Ni_3Ti precipitates is typical to Ti-containing Ni-rich maraging steels, such as C250 and T250 [3–8], Fe-20Ni-1.8Mn-1.6Ti-0.59Al [9], Fe-10Cr-10Ni-2 W [10] and Fe-25.3Ni-1.7 Ti [11] alloys (all concentrations are presented in wt%).

Retained austenite is the untransformed austenite that remains stable after quenching from the austenitizing temperature to room (or subzero) temperature; it is the result of a martensite finish temperature below room temperature, and it generally forms randomly between martensite laths in PH steels. In contrast, *reverted austenite* forms during a subsequent tempering or aging treatment, usually in localized areas. Its occurrence depends on chemical composition, the applied aging temperature and time. In a previous study we reported the formation of reverted austenite during aging of Custom 465® at 480 °C for 4 h [2]. The formation of reverted austenite has been reported for various maraging steels; its morphology is characterized by coarse, patchy regions at martensite lath boundaries [4,8,12]. The orientation relationship between martensite and austenite corresponds to the Kurdjumov-Sachs relationship: a parallelism between the close-packed planes and directions in the two structures. The formation of reverted austenite is the result of a change in the equilibrium concentration of austenite in the alloy. Yet, it is not clear whether this change is solely a function of the temperature, or it is due to local Ni enrichment at temperatures exceeding the stability range of these precipitates. For example, for maraging C250 steel it was demonstrated that the formation of reverted austenite is due to the dissolution of Ni_3Mo precipitates, which locally enrich the matrix with Ni [3].

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According to previous studies [13,14], increasing the aging temperature of Custom 465® results in lower hardness and strength values, while fracture toughness and corrosion resistance are improved. A detailed study of the microstructure evolution upon aging of Custom 465® at different temperatures is essential for the understanding of the relation between aging temperature and the resulting mechanical properties and corrosion behavior. A comprehensive characterization of the microstructure in general, and of potential traps for diffusing hydrogen specifically, is important also for our on-going study of hydrogen permeation through this steel. However, to the best of our knowledge, such thorough characterization is not reported in the literature. Also, the austenite fraction as a function of aging temperature has not been correlated with the evolution of the η-Ni_3Ti phase. To reach these goals, the microstructure of Custom 465® was characterized following aging at temperatures ranging from 482 °C to 648 °C, focusing on the η-Ni_3Ti precipitate dimensions and the fraction of austenite and its location. Dilatometry measurements and thermodynamic calculations were employed to gain a better understanding of the phase transformations occurring during aging treatments.

2. Experimental procedures

2.1. Thermomechanical treatments and microstructure characterization

Custom 465® stainless steel in the form of a 2-inch diameter rod was purchased from Carpenter Technology (Wyomissing, PA). The composition of this steel was determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) analysis as (wt%): Fe–10.7Cr–10.9Ni–0.86Mo–1.4Ti–0.04Al–0.04Zn–0.0046C. The rod was received in the solution annealed (SA) at 900 °C followed by cold-treatment at −73 °C for 8 h within 8 h from the SA treatment. All specimens were cut transversally to the rod axis.

0.5–1.0 mm thick specimens were aged at several temperatures, corresponding to the definition of aging treatments of Custom 465®: 482 ± 5 °C (H900), 510 ± 5 °C (H950), 538 ± 5 °C (H1000), 560 ± 5 °C (H1040), 593 ± 5 °C (H1100), 648 ± 5 °C (H1200). In addition, hardness test was conducted on the 460 ± 5 °C (H860) sample in order to determine the peak hardness. All aging treatments were conducted in an argon shielding atmosphere. Four hours aging durations were chosen, for comparison with other works dealing with the same alloy [13,14]. The heating and cooling rates were 10 °C/min and 40–60 °C/min, respectively, in a tube furnace. During cooling, the samples were drawn away from the heated zone and kept within the furnace atmosphere. Thermocouple was attached to the specimen during all stages of heating and cooling. After aging, the specimens were ground and polished on both sides down to 1 μm. For each treatment, microhardness test was done on 2–3 specimens, with 5 repetitions on each specimen, using Vickers microhardness machine (Shimadzu GmbH HMV-2 T) and 200 g load. The volume fraction of reverted austenite was measured by X-ray diffraction (XRD). A PANalytical Empyrean Powder diffractometer equipped with a position sensitive (PSD) PIXCEL detector and Cu-Kα radiation was used. A graphite secondary monochromator was used to reduce fluorescence effects and improve the signal-to-noise and signal-to-background ratios. The relative quantities of reverted austenite were determined from X-ray diffraction patterns according to standard method ASTM E975 [15] for X-ray determination of retained austenite in steel with near-random crystallographic orientation, using the integrated intensities of X-ray diffraction peaks.

Samples for transmission electron microscopy (TEM) and transmission Kikuchi diffraction (TKD) in a scanning electron microscope (SEM) were mechanically polished to a 30-μm thickness on a 1000 grit SiC grinding paper, and polished with 6 μm and 1 μm diamond pastes. Disks, 3 mm in diameter, were cut by a punch, and the central area of the disk sample was ion-milled to electron transparency using a Gatan Precision Ion Polishing System (PIPS).

JEOL JEM-2100F TEM equipped with an energy-dispersive X-ray spectrometer (EDS) system model JED 2300T was used. Analysis of reverted austenite was done by TKD in a Quanta 200 FEG environmental SEM (ESEM) for orientation mapping, using an Oxford Aztec System with Nordlys II detector.

2.2. Phase transformations – dilatometry

The initial density of the alloy was measured by Archimedes method as 7.777 ± 0.003 g/cm^3. Dilatometry measurements were conducted in order to identify the sequence of phase transformations that take place during aging. Relatively slow heating and cooling rates were assigned in order to achieve conditions which favor thermodynamic stability. The heating rate was 4 °C/min, and the holding time was 30 min at 900 °C, followed by cooling to room temperature at 10 °C/min. The chosen rate of 4 °C/min is a compromise between the low heating rates needed for measurement accuracy (see ASTM E228) and the faster heating rates used for arriving at aging temperature during the thermal treatments. Dilatometry was done using a Linseis-L75 system. The specimen holder and the piston were made of fused silica. The range of extension measurement was ±250 μm. The length, time and temperature information were recorded at microsecond intervals, and the vacuum was attained at 10^{-2} mbar using a rotation pump. Afterward, 1 bar helium atmosphere was filled to facilitate thermal conduction in the instrument. For calibration, the same procedure was followed with pure Fe (99.999%), albeit with a higher initial vacuum of 10^{-5} mbar, using a diffusion pump. Specimens were of 4 × 4 × 20 mm dimensions. The surface was ground on both sides by SiC papers down to 600 grit, followed by polishing down to 1 μm using diamond paste. The parallelism of the measured surfaces was ±0.05 μm.

3. Results

3.1. Microstructure characterization

The changes in hardness, precipitate dimensions and relative volume of reverted austenite upon aging are shown in Tables 1 and 2 and in Fig. 1. Hardness measurements (Table 1) show an increase upon aging relative to the SA condition, from 327 ± 5 VHN in the SA condition to 616 ± 18 VHN in the aged (480–510 °C) condition. As the aging temperature is raised, a lower extent of hardness increase is obtained. In the range 480–550 °C, a decrease in hardness of Custom 465® as the aging temperature is increased has been reported before [13,14].

Selected area electron diffraction (SAED) patterns acquired in the TEM revealed two phases: martensite with a body-centered cubic (BCC) structure and hexagonal η-Ni_3Ti. A representative SAED pattern is shown in Fig. 2. Bright-field (BF) images of aged specimens and their corresponding dark-field (DF) images are shown in Fig. 3. The orientation relationship between the Ni_3Ti precipitates and the martensite matrix was calculated from Fig. 2 as $\{011\}_M//\{0001\}_{Ni3Ti}$ and $\{111\}_M//11\bar{2}0_{Ni3Ti}$. In the BF-TEM images in Fig. 3 one can observe the three variants of η-Ni_3Ti precipitates, at an angle of 60° relative to

Table 1
Vickers hardness measured at 200 g, and after conversion to HRC values. Values are compared to reported measured data.

Aging temp. (°C)	Condition	HVN	HRC[a]	Ref. 13 (HRC)	Ref. 14 (HRC)
460	H860	567 ± 10			
480	H900	615 ± 11	56	54	–
510	H950	616 ± 18	56	54	49.5
538	H1000	548 ± 13	52	52	47.5
560	H1040	547 ± 7	52	51	45.5
593	H1100	481 ± 6	48	–	–
648	H1200	381 ± 6	39	–	–

[a] Converted according to ASTM E140–12.