



Regular article

Precipitation of chromium nitride nano-rods on lamellar carbides along austenite–ferrite boundaries in super duplex stainless steel



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ABSTRACT

In super duplex stainless steel, austenite–ferrite boundaries are preferential sites for the precipitation of chromium nitride (Cr_2N) during heat treatment. In this study, we observed a large number of Cr_2N rods were continuously lined up on a thin lamella of M_{23}C_6 of 20 nm width along an austenite–ferrite boundary. This observation indicates that M_{23}C_6 carbides at the boundary play a significant role in promoting the formation of Cr_2N rods.

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Super duplex stainless steels (SDSS) possess approximately equal amount of austenite (γ) and ferrite (δ) [1,2]. A balanced ratio of the austenite to ferrite phases in SDSS can deliver superior corrosion resistance and mechanical properties [3,4]. Because of these advantages, SDSS have been widely employed in industrial applications such as pipes and pressure vessels as well as subsea flowlines. However, some fabrication processes, e.g. forging and welding, may introduce a list of precipitated phases such as sigma, chi, carbides and nitrides [5–9], which largely degrade the corrosion resistance and mechanical properties [1, 9–20]. One challenge in the fabrication and joining of SDSS components is maintaining a balanced ratio of the austenite to ferrite phases without the precipitates.

Compared with duplex stainless steel (DSS), SDSS has greater additions of Cr and N, which have been shown to improve the corrosion resistance [21]. Resistance to corrosion is ranked according to the pitting resistance equivalent number (PREN_W, taking W into account here) which is determined by $\%Cr + 3.3(\%Mo + 0.5\%W) + 16\%N$ (in weight percentage) [22]. For example, a typical PREN_W of SDSS UNS S32760 (Zeron 100) is approximately 41 while the PREN_W of a DSS UNS S31803 (SAF 2205) is about 35 [1]. In simple terms, the higher PREN_W of SDSS provides the capacity to serve in more corrosive environments [22]. However, one drawback of the higher Cr and N content of SDSS is the tendency for the precipitation of nitrides, especially

nanoscale Cr_2N rods which can locally degrade the corrosion resistance [13–15]. Many studies have investigated the mechanism of Cr_2N precipitation in SDSS, and it is generally agreed that the austenite–ferrite boundaries are preferential sites for Cr_2N to nucleate, owing to a mismatch in microstructure that occurs at the boundaries, which results in a lowering of the energy barrier for the diffusion of N and Cr atoms [5,23,24].

To investigate the Cr_2N precipitation in SDSS, a sample extracted from a UNS S32760 flowline was used, the chemical composition of which (in weight percentage) is: 0.02% C, 0.45% Si, 0.49% Mn, 0.002% S, 0.022% P, 24.7% Cr, 6.8% Ni, 3.65% Mo, 0.7% W, 0.72% Cu, 0.23% N with the balance as Fe. The sample was solution heat treated for 1 h at 1200 °C followed by aging at 800 °C for 30 min, with water quenching to precipitate Cr_2N . Scanning electron microscopy (SEM) sample was prepared to a 0.04 μm colloidal silica finish, and then was analysed using a FEI Sirion 200 SEM at 20 kV. The sample for transmission electron microscopy (TEM) was prepared using a double-jet electropolisher with an electrolyte consisting of a mixture of 5 wt% perchloric acid and 95 wt% ethanol. The TEM experiment was performed on a JEOL 2100F at 200 kV equipped with a scanning transmission electron microscopy (STEM) detector. A double tilt sample holder was engaged to rotate the sample in the TEM. Energy dispersive X-ray spectroscopy (EDS) was used for semi-quantitative chemical analysis.

The morphology of the rod-shaped precipitates at an austenite–ferrite boundary is shown in Fig. 1 and Fig. 2, using STEM and SEM, respectively. Fig. 1 shows a large number of rod-shaped precipitates that were continuously lined up along an austenite–ferrite phase boundary

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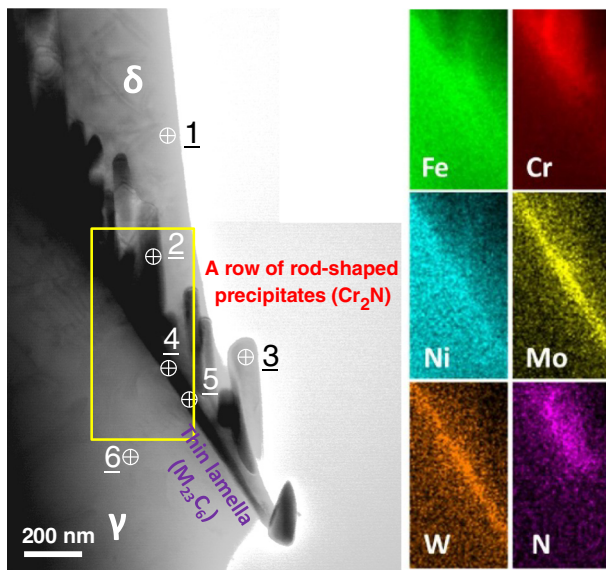


Fig. 1. STEM observation of rod-shaped precipitates on a thin lamellar precipitate, and the corresponding EDS examination results are shown in Table 1; EDS mapping, results on right side, was performed to examine the highlighted area (yellow box). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

observed in STEM mode, and remarkably, a thin lamella adjacent to these rods. A similar morphology was also observed by SEM observation which is shown in Fig. 2. Ferrite (where SEM-EDS point 1 located) is on left top side and austenite (where SEM-EDS point 2 located) is on the bottom right side. A row of dark, rod-shaped precipitates (where SEM-EDS point 3 located) is clearly observable at this austenite-ferrite phase boundary.

According to the SEM-EDS results in Table 1, typical chemical compositions of ferrite and austenite were measured. Besides, SEM-EDS spot examination on rod-precipitate shows a ~ 31 wt.% Cr content. This result implies the precipitate has high Cr content since the diameter of the spherical volume of excitation during EDS is about 1 μm , which therefore includes the X-ray signals from both precipitate and ferrite matrix.

More quantitative STEM-EDS points and mapping measurements were performed to examine the rods and lamella precipitates chemical compositions, and results are shown in Table 1 and Fig. 1, respectively. According to STEM-EDS point results, high Cr (72.1 wt.% maximum) was measured in rod-shaped precipitates, moreover, a high N was

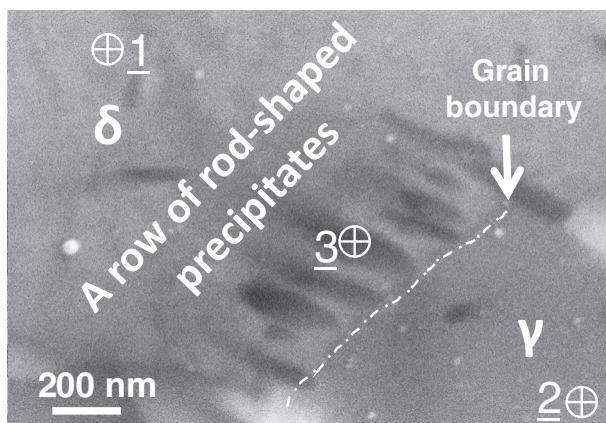


Fig. 2. SEM image, showing a row of rod-shaped precipitates along an austenite-ferrite boundary. The corresponding EDS examination results are shown in Table 1.

Table 1
SEM-EDS and STEM-EDS results

Method	Spot	Elements (Wt.%)					Position
		Fe	Cr	Ni	Mo	W	
SEM-EDS	1	63.0	27.2	5.1	4.7	–	δ
	2	63.5	24.2	8.5	3.7	–	γ
	3	58.8	31.2	3.8	4.7	–	Rods (Cr_2N)
STEM-EDS	1	58.2	29.2	5.1	3.9	0.8	δ
	2	34.0	54.8	2.9	4.1	0.7	Rods (Cr_2N)
	3	18.1	72.1	1.4	4.0	–	Rods (Cr_2N)
	4	49.6	25.9	5.4	12.0	4.0	Lamella (M_{23}C_6)
	5	49.7	27.6	5.8	10.4	3.2	Lamella (M_{23}C_6)
	6	60.9	26.1	7.7	2.7	–	γ

shown in local rods according to STEM-EDS mapping result. These typical chemical content and morphology suggest these rod-precipitates are Cr_2N . However, this thin lamella cannot be identified with the single EDS results though a high Mo (>10 wt.%) and W (~4 wt.%) was measured. Here, high resolution (HR) TEM was performed to identify their lattice structure.

The TEM sample was rotated to ferrite $[\bar{1}11]$ zone axis in conventional TEM mode to reveal the detailed structure of this phase boundary, see Fig. 3 (a). An enlarged view of this thin lamella, area marked in a yellow box in Fig. 3 (a), is shown in Fig. 3 (b). By measuring the atomic planes spacing, this thin lamella is identified as M_{23}C_6 , and a width of ~20 nm is measured for it.

High resolution images of Cr_2N , M_{23}C_6 and δ phases are then obtained individually and shown in Fig. 3 (c–e) by which the orientation relationship of Cr_2N and M_{23}C_6 with ferrite is determined as:

$$(0002)\text{Cr}_2\text{N} \parallel (400)\text{M}_{23}\text{C}_6 \parallel (110)\delta$$

$$[\bar{1}100]\text{Cr}_2\text{N} \parallel [01\bar{1}]\text{M}_{23}\text{C}_6 \parallel [\bar{1}11]\delta$$

This is the first report of the orientation relationship between Cr_2N and M_{23}C_6 . Selected area diffraction was applied to further determine the orientation relationship between austenite and these phases. Fig. 4 (a) shows selected areas of ferrite and austenite along this phase boundary. Fig. 4 (c) shows an asymmetrical austenite selected area diffraction patterns (SADP) when the incident beam direction is in $[\bar{1}11]\delta$ zone axis. After a 3.2° rotation of the TEM sample about $g = 3\bar{1}1$, a symmetrical $[\bar{1}14]$ austenite SADP was obtained, see Fig. 4 (d). Fig. 4 (e) is a schematic representation of the ferrite and austenite diffraction pattern. Thus, the orientation relationship between ferrite and austenite can be determined:

$$(202)\delta \parallel (3\bar{1}1)\gamma \text{ and } [\bar{1}11]\delta \parallel [\bar{1}14]\gamma, \text{ with } 3.2^\circ \text{ misorientation}$$

This orientation relationship suggests this is a typical austenite-ferrite phase boundary [25,26]. For the orientation relationship between austenite and M_{23}C_6 , in the scope of authors' knowledge, the only reported by previous studies is $(11\bar{1})\gamma \parallel (11\bar{1})\text{M}_{23}\text{C}_6$ and $[011]\gamma \parallel [011]\text{M}_{23}\text{C}_6$ [6,23,24,27,28]. Therefore, it appears as though this M_{23}C_6 carbide has no direct orientation relationship with austenite phase, which means austenite playing an insignificant role in its formation. Considering the isothermal heat treatment applied at 800°C in this study, the local phase transformation $\delta \rightarrow \text{M}_{23}\text{C}_6 + \text{Cr}_2\text{N}$ is reasonable since the phase transformation at 800°C arise dominantly from ferrite while it is relatively inertion for austenite.

Though the presence of lamellar M_{23}C_6 on the boundary plays a significant role on the formation of Cr_2N in this study, the misfit observed in this isolated case is unlikely to be representative of all boundaries. Therefore, a further investigation is needed to reveal the relationship between the misfit of boundaries and the precipitation of lamellar M_{23}C_6 .

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