Characteristics of Flakes Stacked Cr$_2$N with Many Domains in Super Duplex Stainless Steel

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Abstract: This study mainly observed the Cr$_2$N (chromium nitride) nucleation and growth in SAF 2507 duplex stainless steel. However, the investigation revealed that Cr$_2$N has a complex substructure separated into many regions. In SAF 2507 duplex stainless steel, Cr$_2$N nucleated at the dislocations and the precipitates were composed of many Cr$_2$N flakes gathered together when aged at 600 °C.

Keywords: super duplex stainless steel; chromium nitride; dislocation

1. Introductions

Duplex stainless steels (DSS) have been widely used as structural materials in the power, chemical and oil industries [1–3]. The beneficial mixture of austenitic (γ) and ferritic (δ) properties in the duplex microstructure (δ + γ) results in high strength with desirable toughness [4], combined with a good corrosion resistance, especially against chloride-induced pitting and crevice corrosion, as well as stress corrosion cracking [5–7]. The heat treated SAF 2507 DSS can lead to a series of transformations in the ferrite matrix or at the interphase boundaries, in addition to the martensite forms from the austenite [8,9]. In a previous study [10], the different new phases and precipitates of the δ-ferrite matrix decomposition were characterized in the temperature range of 400–1050 °C. The phase transformation in DSS always takes place in ferrite rather than in austenite for two reasons. First, the atomic density is lower in the lattice of ferrite than in the lattice of austenite; second, the enriched chromium (Cr) and molybdenum (Mo) in the ferrite phase is favorable for interphase nucleation [10]. The characterization of the phase precipitates is best performed on isothermally heat-treated samples with a fully δ-ferrite microstructure retained by water quenching to room temperature. This isothermal treatment induces the decomposition of the supersaturated δ-ferrite and produces various phases: M$_{23}$C$_6$ and M$_7$C$_3$ carbides [8], secondary austenite formed as Widmannstätten precipitates [11], δ-ferrite decomposed to secondary austenite (γ2) with σ phases via the eutectoid reaction [12,13], τ phase [14], R phase [15], σ phase [16,17] and χi (χ) [17,18] phase. The intermetallic χ-phase, whose characterization is reported in the present paper, is a tetrahedral close-packed (TCP) phase.

The presence of this phase was reported for the first time by Andrews and Brookes [19] in a steel containing Cr, Ni and Mo. McMullin et al. [20] have also found the presence of an equilibrium phase of this intermetallic compound in the temperature range of 815–900 °C as isothermal sections of the
ternary diagram for Fe-Cr-Mo. Intermetallic phases ($\chi$ and $\sigma$) and Cr$_2$N precipitate in grains or at phase boundaries during slow cooling in the critical temperature range of 1000 °C (1273 K) to 700 °C (973 K). Another aspect is that a high density of chromium nitrides is generated in the interior of the ferrite grains as a result of super-saturation with nitrogen by rapid cooling from high temperatures by quenching [21]. As the nitrogen solubility in ferrite is quite low, it leads a super-saturation of nitrogen in ferrite [22].

A stimulating effect on sigma phase precipitation in DSS can be achieved by cold working prior to aging. The microstructures in deformed steels, similar to the un-deformed steels, exhibit the transformation of ferrite phase into a mixture of secondary austenite and sigma phase [23,24]. In the meantime, its amount is increased by the nitrogen content [25]. The nucleation sites of sigma are the incoherent twin boundaries, grain boundaries and the intra-granular dislocations [26]. Accidentally, it also nucleates at coherent twin boundaries [23]. A key point to point out is that Cr$_2$N is found in the range of 700–900 °C, somewhat lower temperatures, whereas $\sigma$ phase forms essentially in the temperature range of 800–1010 °C. Another remarkable feature is the intermetallic R phase precipitates after aging at 700 °C for 3 h, but dissolves after longer aging times, the intermetallic R phase was not observed after 72 h and no evidence of any carbides of any different type was found [26]. The substantial amounts of N caused the grain boundary Cr$_2$N, which often formed in cooperation with secondary austenite [26]. As $\delta$-ferrite decomposes to $\sigma$ and $\gamma_2$ phases, Cr migrates to the $\sigma$ phase and N is absorbed by the $\gamma_2$ phase via the eutectoid decomposition process. After a certain duration of aging, the $\delta$-ferrite completely decomposes, causing the growth of $\sigma$ phase to stop. Finally, the positions of primary $\delta$-ferrite are collectively occupied by the $\sigma$ and $\gamma_2$ phases [27].

The Cr$_2$N epsilon phase co-exists along with secondary austenite and the sigma phase at temperatures below 950 °C. The literature of TEM studies have revealed the two morphologies of inter-granular and intra-granular Cr$_2$N precipitates. Ductility deteriorates with a rise in yield strength simultaneously as the aging time increases [28]. In the meantime, it has a reduction in the toughness and corrosion properties too [29]. Particularly at 475 °C, with aging times greater than 17 h, this aging treatment at low temperature can cause a significant reduction in the impact strength and toughness of DSS 2205 [30]. Precipitates of Cr$_2$N exist at $\delta/\delta$, $\delta/\gamma$ phase boundaries and within the $\delta$ ferrite matrix after water quenching from a high solution temperature. Nevertheless, these Cr$_2$Ns in the form of lath-shaped crystals are distributed at the $\delta$ ferrite sub-grain boundaries [31].

From the preceding welding study [32], there were many Cr$_2$N precipitates found in the $\delta$ ferrite of super DSS. This gives rise to the motivation to investigate the nucleation and growth of the Cr$_2$N microstructural evolution in its early stage for this super DSS during aging. At present, no report discloses details of the mechanism of Cr$_2$N nucleation and growth.

2. Materials and Methods

Fe-0.01C-0.37Si-0.65Mn-23.9Cr-6.53Ni-0.19Co-3.74Mo-0.31Cu-0.03N in wt.% is the chemical composition of SAF 2507 DSS as determined with a glow discharge spectrometer (GDS). The samples were heated at 750 °C with a holding time of 5 h, or at 600 °C with holding times in a series of 5, 10, 30, 60, 90 min, and 7 h, respectively, then they were water quenched after aging.

The foils examined under the transmission electron microscope (TEM) in a model of FEI Tecnai G2 F30 were prepared using the following procedure: the specimens were thinned to a thickness of 0.2 mm with #400 sandpaper and further thinned to 0.1 mm with #800 sandpaper before being electro-polished with a twin jet at 45 V in a solution of 5% perchlorate, 25% glycerin, and 70% ethyl alcohol at −5 to −10 °C. Punched 3-mm diameter disks were further thinned to 0.05 mm with #1200 sandpaper.
3. Results and Discussion

3.1. Cr₂N Transformation at 600 °C under 7 h Holding in SAF 2507

The microstructural details of Cr₂N precipitation in δ ferrite were investigated by transmission electron microscopy (TEM). Two typical shapes of coarse Cr₂N precipitates were revealed in Figure 1, the precipitates at the phase boundary were mostly needle shapes with a particular crystal orientation relationship (OR) to the matrix and the others were within the grains after the relatively long time of aging of 7 h at 600 °C. Cr₂N dispersely precipitated within the δ ferrite in specimens aged at 600 °C for 7 h. The selected-area diffraction patterns, which were obtained from the interfacial regions of the Cr₂N and δ phase, as shown in Figure 1, indicated a characteristic orientation relationship between Cr₂N and the δ phase. A dispersion of finer precipitates of Cr₂N existed within the δ ferrite grain, although coarser nitrides are distributed mainly as stacks along the ferrite sub-grain boundaries. It seemed that the favored heterogeneous nucleation at sub-grain boundaries or dislocations determined the variation in nitride size [33].

![Figure 1](image.png)

**Figure 1.** Microstructure of a specimen aged at 600 °C for 7 h (a) transmission electron micrograph showing Cr₂N precipitated within δ-ferrite; (b) diffraction pattern with zone [011]_δ∥[121]_Cr₂N; (c) interpretation of (b); (d) Cr₂N formed at phase boundary.

3.2. The Detailed Substructure of Cr₂N

Figure 2a is a micrograph of Cr₂N precipitated at 600 °C after 7 h holding, and Figure 2b presents a high magnification image of Figure 2a. Figure 2c is the micrograph of Cr₂N precipitated at 750 °C after 5 h holding, and Figure 2d presents a high magnification image of Figure 2c. What is interesting is that Cr₂N in the high magnification images has many fringes in it (Figure 2b), and even two fringe directions can be observed (Figure 2d). The substructure within Cr₂N is visible. Furthermore, the further high magnification of Cr₂N precipitated at 750 °C after 5 h of holding shows that Cr₂N is not as simple as we have seen. The fact is that Cr₂N is composed of many different domains (Figure 3a), which are further separated into different regions, as illustrated by the HRTEM or HREM (High-resolution transmission electron microscopy) image (Figure 3b).
Finally, after 7 h, Cr$_2$N flakes stacked together to form needle-like crystals. The tiny Cr$_2$N nucleated at the dislocations after 10 min (Figure 4b,c). After 30 min, Cr$_2$N rods or CrN plates followed a kinetic “C” curve to precipitate from the ferrite by nucleation and growth [34]. Dislocations, inclusions, grain boundaries (δ/δ), and interphase interfaces (δ/γ) were the locations for Cr$_2$N nucleation, growth and coalescence is shown in Figure 3. In order to display Cr$_2$N nucleation very clearly, the dark-field images (DFI) in Figure 4c–h were utilized by tilting the sample until it satisfied the invisible condition of g vector dot burger vector b equal to zero (g · b = 0), to eliminate the most dislocations, as the size of nucleated Cr$_2$N was too small and thin to obtain diffraction spots. The sequence of Cr$_2$N nucleation, growth and coalescence is shown in Figure 4a–i. Cr$_2$N nucleated at the dislocations appeared as stacks of several small flakes in parallel (Figure 4g,h) or two mutually perpendicular flakes (Figure 4f). To clarify the mechanism of Cr$_2$N nucleation and growth in the δ phase of DSS, SAF 2507 was heated to 600 °C for different aging times. At 600 °C, the dislocations appeared in the δ phase after 5 min (Figure 4a). The tiny Cr$_2$N nucleated at the dislocations after 10 min (Figure 4b,c). After 30 min of holding, Cr$_2$N gradually grew into flakes, and a large amount of Cr$_2$N flakes were distributed within the α matrix (Figure 4d–h). Finally, after 7 h, Cr$_2$N flakes stacked together to form needle-like Cr$_2$N (Figure 4i). It is notable that the two directions of Cr$_2$N flake growth were along the (020) plane and the (002) plane, and the Burgers vector of the dislocation loops, which were tangled with the Cr$_2$N flakes, was 1/2 < 111 >, as shown in Figure 4e. During rapid cooling from the δ ferrite field, the microstructure consisted of large ferrite grains with a low amount of allotriomorphic and Widmanstätten austenite and abundant intra-granular nitrides [34]. These Cr$_2$N rods or CrN plates followed a kinetic “C” curve to precipitate from the ferrite by nucleation and growth [34]. Dislocations, inclusions, grain boundaries
(δ/δ), and interphase interfaces (δ/γ) were the locations for nucleation of Cr2N rods. The corrosion resistance and toughness of DSSs were sacrificed severely by the Cr2N precipitation [34].

Figure 4. The sequence of the Cr2N nucleation and growth mechanism at 600 °C. (a) 5 min for only lattice defects of dislocation, (b,c) 10 min for Cr2N nucleated at dislocations, (d–h) 30 min for Cr2N flakes either stacked mutually perpendicular or stacked parallel together, (i) 7 h for Cr2N flakes coalescence.

4. Conclusions

There are two morphologies for Cr2N nucleation and growth. One precipitation occurs at grain or phase boundary and forms the micrometric size Cr2N that are mostly needle shapes with a particular crystal orientation relationship (OR) to the matrix. Another precipitation occurs within the matrix and forms the nanometric size Cr2N composed of flakes, or of many orientation domains. Cr2N first nucleated in multiple positions at dislocations and gradually grew into many flakes, which grew in perpendicular or in parallel. Furthermore, the Cr2N flakes interacted with dislocation loops. At longer holding times, dislocations were discharged and the Cr2N finally coalesced and eventually grew into complete needle-like Cr2N with many domains.

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