Inhibition of Nitride Precipitation in a Fe-Cr-Mn-Mo-N High-Nitrogen Austenitic Stainless Steel through Grain Boundary Character Distribution Optimization

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Abstract. The precipitation behavior of the second phase in Fe-18Cr-17Mn-2Mo-0.85N high nitrogen and nickel-free austenitic stainless steel after grain boundary character distribution (GBCD) optimization was investigated. The results show that the fraction of low Σ coincidence site lattice (CSL) boundaries increases from 47.9% for the solid solution treated specimen to 82.25% for the specimen cold-rolled by 5% and then annealed at 1423 K for 72 h (r5%-a1423 K/72 h). Compared with the solution treated sample, nitride precipitation is obviously restrained and the fraction of precipitates is the least in r5%-a1423 K/72 h sample with the highest proportion of SBs. The appearance of a high proportion of CSL boundaries with low energy inhibits the nitrides precipitation through GBCD optimization.

1. Introduction
Austenitic stainless steel (ASS) is a kind of steel with austenitic structure at high temperature and room temperature without structural transformation. It has been widely used in various fields because of its good mechanical property and corrosion resistance. However, the severe shortage of nickel resources and the allergic reaction when it applied to the human body have advanced the development of high nitrogen austenitic stainless steel (HNASS)[1]. As an interstitial element, nitrogen dissolved in solid solution is beneficial for increasing the strength without significant losses of the toughness and ductility of ASS[2]. In addition, it can improve the localized corrosion resistance while saving the cost of ASS. Therefore, great attention is now focused on HNASS.

However, the nitrides may precipitate at the grain boundary when exposed to temperatures between 973 K–1223 K[3], which will severely damage the properties related to the grain boundary, and then the application of HNASS will be restricted. It has been reported that nitrogen enlarges the Cr₂N precipitation zone and increases the sensitivity to intergranular corrosion (IGC) in low carbon steels containing nitrogen in the range of 0.02–0.54%[4].

Solution treatment is often used to re-dissolve the second phase. However, it is difficult to treat the extreme structural parts due to the limitation of the size of heat treatment furnace. Moreover, it is still necessary to avoid the sensitized temperature range after treatment. Watanabe[5] firstly proposed the concept of "grain boundary design and control" in 1984. It pointed out that the number and distribution of coincident site lattice (CSL) may be increased or changed in the grain boundary character distribution (GBCD) through proper technology, which will improve the overall performance of alloy. And it is
described as grain boundary engineering (GBE) some years later. A large number of special boundaries (SBs) can be obtained through thermo-mechanical processing and GBCD can be optimized. Jones[6] investigated that GBE significantly reduced the degree of sensitization of 304 austenitic stainless steel exposed at 923 K for 4 h by means of increasing the Σ3 and Σ9 boundaries.

Research on the application of GBE to HNASS is rarely reported. The present work explores the effect of GBE technology on precipitation along the grain boundary in HNASS in order to solve the problem of grain boundary failure caused by the precipitation of the second phase.

2. Experimental Procedures
The chemical composition of experimental steel was listed in Table 1. The sheet was solution-annealed at 1323 K for 1 h, followed by water quenching (WQ), which was marked as the base materials (BM).

| Table 1. Chemical composition of experimental steel (wt%). |
|------------------|---------------|----------------|--------------|----------------|----------------|
| Cr   | Mn     | Mo      | N   | C   | Fe                     |
| 18.36 | 16.52  | 2.32   | 0.85 | 0.023 | Balanced              |

After the solution treatment, BM samples were cold rolled by 5% and then annealed at 1423 K for 10 min or 72 h, following by WQ, which are called r5%-a1423 K/10 min and r5%-a1423 K/72 h, respectively. Sensitization treatment was made by annealing at 1123 K for 1 h and 2 h. The metallographic microstructure was observed by Olympus GX 71 optical microscopy (OM). Low-ΣCSL boundaries (Σ≤ 29) were identified by Brandon criterion [7].

3. Results and discussion
Figure 1 shows the optical microstructure of BM sample. It can be seen that the microstructure of BM sample is single-phase austenite with some annealing twins.

Figure 2 shows the optical microstructures of BM, r5%-a1423 K/10 min and r5%-a1423 K/72 h samples respectively sensitized at 1123 K for 1 h or 2 h. The discontinuous precipitates indicated by the arrows in Figure 2 (a). With the annealing time increasing, the precipitates grow with a cellular way towards the grain, indicated by the arrows in Figure 2 (b). According to our previous research results, the precipitates are identified Cr2N phases[8, 9]. From Figure 2(c)-(f), it can be seen that the precipitation is obviously inhibited in the GBE treatment samples. In the r5%-a1423 K/72 h samples (Figure 2 (e) and (f)), the degree of inhibition of the precipitates is the best.
Figure 2. The optical microstructures of different samples sensitized at 1123 K for different times (a) BM-1 h; (b) BM-2 h; (c) r5%-a1423 K/10 min-1 h; (d) r5%-a1423 K/10 min-2 h; (e) r5%-a1423 K/72 h-1 h; (f) r5%-a1423 K/72 h-2 h.

In order to examine the effect of the GBE technology on the degree of Cr2N precipitation along grain boundaries, a detailed EBSD analysis and the fraction of precipitates conducted. The relationships between the fraction of SBs and degree of precipitate are summarized in Table 2. It can be found that the fraction of precipitates is the least in the sample with the highest proportion of SBs.

Table 2. The fraction of SBs and precipitates sensitized at 1123 K for different times in different samples.

| Samples                 | Total SBs(%) | The fraction of precipitate (%) sensitized at 1123 K for 1 h | The fraction of precipitate (%) sensitized at 1123 K for 2 h |
|-------------------------|--------------|------------------------------------------------------------|------------------------------------------------------------|
| BM                      | 47.9±1.8     | 3.1±0.4                                                    | 8.5±0.7                                                    |
| r5%-a1423 K/10 min      | 66.5±2.9     | 0.3±0.1                                                    | 0.7±0.3                                                    |
| r5%-a1423 K/72 h        | 82.25±1.02   | 0.2±0.05                                                   | 0.4±0.08                                                   |

Several researchers[10-12] have studied that the carbides have a high tendency to precipitate at the general high angle boundaries (GHABs) than low-ΣCSL grain boundaries. Figure 3 shows the OM microstructures and the corresponding EBSD analysis results. From Figure 3, it can be seen that all GHABs are occupied by precipitates easily and no precipitate is observed along all coherent Σ3 boundaries (Σ3c), therefore, it is apparent that the Cr2N precipitation strongly relates with the type of grain boundaries and it tend to precipitate at GHABs than SBs indicated by the corresponding arrows in Figure 3 (a-d). These GHABs with high energy provide more favorable sites for the formation of precipitates in BM sample (Figure3 (a)). During thermo-mechanical processing, a large number of SBs (especially annealing twins) with low energy generated in GBE samples, which makes precipitation suppressed in the r5%-a1423 K/72 h sample compared BM sample (Figure 3 (a), (b) and Table 2), which confirming the GBE technology plays a vital role in suppressing the precipitation of Cr2N along
grain boundaries.

In other words, the formation of a large number of SBs is the key to the suppression of nitride precipitation in the experimental steel. Therefore, it is foreseeable that the suppression of nitride precipitation through GBCD optimization can improve the properties of materials related to grain boundaries, for example, IGC property, intergranular stress corrosion cracking (IGSCC) property and corrosion fatigue property etc. in HNASS.

Figure 3. OM image of microstructures and corresponding EBSD analysis of BM (a, c) and r5%-a1423 K/72 h sample; (b, d) sensitized at 1123 K for 2 h.

4. Conclusions
In the experimental steel 18Cr-17Mn-2Mo-0.85N, the fraction of low ΣCSL boundaries increases from 47.9% for the solid solution treated specimen to 82.25% for the specimen cold-rolled by 5% and then annealed at 1423 K for 72 h. Compared BM sample, the second phase precipitation is obviously suppressed after GBCD optimization. The fraction of precipitates is the least in the 1423 K for 72 h sample with the highest proportion of SBs.

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