Effect of Boron Addition on the Precipitation Behavior of S31254

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Abstract: To reduce the precipitation of \(\sigma\) phases and to improve the hot workability of S31254 steels, boron has been added into the composition of S31254 to a concentration of 40 ppm. The precipitation behavior was investigated before and after the addition of boron in different S31254 alloys during the compression deformation, and the nose temperature at 950 °C and the phase dissolution temperature at 1074 °C were selected as the measurement temperature. The result showed that more \(\sigma\) phases were precipitated at the grain boundary of S31254 alloys, compared to the boron-added alloy. Meanwhile, the addition of 40 ppm boron into the alloys has obviously prevented the \(\sigma\) phases from the austenitic matrix, and it takes longer time for the precipitation of \(\sigma\) phase at 950 °C. The specific influence factors of boron on the precipitation of \(\sigma\) phases were also further discussed.

Keywords: \(\sigma\) phase; super austenitic stainless steel; precipitation mechanism; compression deformation; boron

1. Introduction

S31254 steel with high content of Cr, Ni, Mo and N, known as a kind of super austenite stainless steel, is widely used in seawater treatment systems, chemical processing equipment, flue gas desulfurization systems, incinerators, and the nuclear industries, due to its excellent corrosion resistance [1–3]. Generally, the S31254 has a face centered cubic (FCC) structure [4–7]. Moreover, due to its high Mo and Cr content, brittle harmful precipitates such as carbide, \(\chi\) and \(\sigma\) phases, can be easily formed [8–11], leading to the deterioration of the corrosion resistance and mechanical properties. The solution and precipitation of second phases are often relative to the local composition, heat treatment time and temperature [12–19]. As temperature changes from 700 °C to 1100 °C, carbides can easily form. Also, these carbides are usually replaced by intermetallic compounds at longer aging times, such as \(\sigma\), \(\chi\) and Laves phases. Low carbon solubility can lead to the formation of \(\sigma\) phase, while a high solubility of interstitial elements in the austenite matrix favors the precipitation of \(\chi\) and Laves phases. The increased Mo content is helpful for the precipitation of intermetallic compounds at higher temperatures. Therefore, it is very important to avoid the existence of a brittle phase.

As an efficient method, the segregation of B atoms at the austenite grain boundary can lower the grain boundary energy, and inhibit the nucleation of second phase. The positive effects can be obtained only by a very small amount of B, within the order of ppm, providing significant impacts on the production process of steels [20]. For example, Sadahiro Yamamoto and Yasuo Kobayashi...
have studied the influence of heat deformation of Ni and B in austenite stainless steel with high Mo. They found that B can reduce the segregation of P and S in the grain boundary area, and the hot workability can be improved [21]. Ueno et al. reported that Mo exhibited a combined addition effect with B, leading to the increase of hardenability, whereas other elements such as Si, Mn, and Cr did not show such a combined effect [22]. The Mo-B synergetic effect was also sensitive to the B content and heat treatment temperature. The combined effect of Mo-B may be caused by the retardation of B precipitation M$_2$3(CB)$_6$ [23]. As per the effect of boron additions on the phase transformation temperatures and precipitation processes, it is also valuable to explore the influence on precipitation behavior by boron in S31254 during the heat deformation process.

In this work, S31254 alloys with and without boron are prepared and chosen as experimental materials, and hot compression with different deformation degrees was carried out to investigate the precipitation of phase at the 950 °C and 1074 °C. Finally, the effect of boron on the inhibition of $\sigma$ phase was clarified.

2. Materials and Methods

2.1. Materials

According to the ASTM A312, the alloys were melted in the vacuum induction furnace and their composition was shown in Table 1. The ingots were first hot rolled to 12 mm plate in thickness. Then, solution treatment was carried out and the process route is shown in Figure 1. The pickling followed to remove the oxide scales and samples with a size of $\Phi 8 \times 10$ mm are made for thermo-compression.

### Table 1. Chemical compositions of experimental alloys (wt %).

| No.          | C   | Si  | Mn  | P   | S   | Cr  | Ni  | Mo  | Cu  | N   | B   |
|--------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| S31254       | 0.010 | 0.610 | 0.430 | 0.024 | 0.001 | 20.180 | 18.000 | 6.000 | 0.690 | 0.193 | 0.000 |
| S31254-B     | 0.014 | 0.620 | 0.940 | 0.014 | 0.006 | 20.150 | 18.110 | 6.120 | 0.720 | 0.200 | 0.040 |

**Figure 1.** Solution treatment diagram of experimental alloys.

2.2. Experimental Procedures

Thermo-Calc software 2015b (Thermo-Calc Software, Solna, Sweden) was utilized for the design of alloys with the database is TCFE6 [13]. Thermo-compression of the alloys was tested by the Gleeble3800 hot simulation experiment machine (Dynamic Systems Inc., Segundo, MD, USA) at 950 °C and 1074 °C, with a compression deformation rate of 10%, 20% and 40%, respectively. The specific experiment processes were as follows. The specimens were heated up to 1200 °C at the speed of 10 °C/s, held for 4 min and cooled down to 1074 °C and 950 °C, and compressed at the speed of 0.1 s$^{-1}$ after holding for 30 s. Then metallographic preparations with customary operations were taken and chemically etched with “Aqua Fortis” for 30 s (concentrated hydrochloric acid and concentrated nitric acid ratio of 3:1). The microstructure was observed by a Leica DMR microscope (LEICA, Shanghai Optical Instrument Factory, Shanghai, China) and LEO438VP Scanning Electron Microscope (SEM, Carl
Zeiss Jena, Oberkochen, Germany). The precipitations were analyzed by JEM-2100(HR) Transmission Electron Microscope (TEM, JEOL, Tokyo, Japan) and Simultix 12 model X-ray diffraction Spectrometer (XRD, Scienscope, State of California, CA, USA) at a scanning speed of 2°/min ranging from 20° to 80° with Mo Kα.

3. Results and Discussion

3.1. Kinetics of σ Phase Precipitation

Figure 2 shows the phase equilibrium diagrams of S31254 and S31254-B by Thermo-Calc software, where some main precipitates such as σ, χ and M23C6 phases can be found. Compared to other precipitates, the σ phase has a relatively higher content, which may affect the properties of alloy more. According to Figure 2a,b, the σ phase totally dissolves in the S31254 matrix at 1073.531 °C, but in the S31254-B alloy at 1073.143 °C, which means the addition of boron has little effect on the σ phase dissolving temperature. Also, a similar law can be found for the χ and M23C6 phases. Figure 3 further shows the isothermal transformation diagram (TTT) in S31254 and S31254-B steels. The nose temperature of the alloy without B is 890 °C, and σ phase just needs to be precipitated only about 3 min. However, after addition of 40 ppm boron, the nose temperatures decreased to 865 °C and it takes 10 min for the critical temperature to precipitate σ phase. Therefore, the TTT shifts to the right after the boron addition, suggesting that the addition of boron inhibits the precipitation of σ phase and narrows the sensitive temperature range.

Figure 2. Thermodynamic calculation results of experimental alloys which are calculated by Thermo-Calc: (a) and (b) S31254, (c) and (d) S31254-B.
Figure 3. The isothermal transformation diagram (TTT) in S31254 and S31254-B.

3.2. Stress Strain Curve

Figure 4 shows the stress-strain curves of S31254 and S31254-B alloys at 950 °C and 1074 °C, respectively. Obviously, the deformation strength of S31254-B is higher than S31254 under the same compression conditions. As shown in Figure 4a, the deformation strength of S31254-B is 50 MPa, 20% higher than S31254 at 950 °C. Also, a whipsaw-shape fluctuation in the curve was observed when the deformation reached 30%. Further, the deformation strength increases by 25 MPa after the boron addition at 1074 °C (Figure 4b). Hence, the addition of boron increases the deformation strength of the alloy. The whipsaw-shape fluctuation in the curve was not found when the compression test was done at 1074 °C, which may be related to the dissolution of σ phase.

Figure 4. The stress-strain curves for S31254 and S31254-B at different temperatures with strain rates of 0.1 s⁻¹; (a) 950 °C, (b) at 1074 °C.

3.3. Microstructure Evolution

Figure 5 shows the microstructure of the alloys after solution treatment at 1200 °C. In order to characterize the precipitates in S31254, EDS analysis was carried out and shown in Figure 6. A little small σ phase can be found inside the grains and around the grain boundary in S31254, but no σ phase was seen in the austenite matrix of S31254-B. The elements such as Fe, Si, Cr, Mo, Ni and so on can be found in S31254 matrix (Figure 6a), and the Mo and Cr are 7.87 and 20.92 wt % respectively. However, the Mo and Cr with a 19.85 and 24.89 wt % contents in the precipitation, confirmed the formation of σ phase based on the increased Mo and Cr composition. Moreover, it can be speculated that the addition of boron into S31254 influenced the dissolving temperature and the precipitation amount of σ phase. Figure 7 further shows the TEM images and SAED patterns for the matrix and precipitates phase of S31254. As shown in Figure 7, very fine granular black precipitates were observed at the grain boundaries, besides the matrix structure. The lattice constant in the
matrix (Figure 7a) is \(a = b = c = 3.66 \text{ Å}\), which belongs to the face-centered cubic austenite structure. However, the lattice constant in precipitates (Figure 7b) is \(a = b = 8.96 \text{ Å}\) and \(c = 4.64 \text{ Å}\), corresponding to the \(\sigma\) phase structure from the previous work [23–25].

![Figure 5](image1.png)

Figure 5. SEM micrograph of the experimental alloys after solution treatment: (a) S31254, (b) S31254-B.

![Figure 6](image2.png)

Figure 6. EDS analysis of microstructure of S31254 after solution treatment: (a) \(\gamma\) substrate, (b) precipitate.

Here 950 °C is the finish rolling temperature and nose temperature of \(\sigma\) phase in S31254, and 1074 °C is the dissolving temperature of \(\sigma\) phase; the thermo-compression tests were carried out on both alloys at 950 and 1074 °C, in order to study the precipitation behavior of \(\sigma\) phase under different deformation in S31254 and S31254-B alloys. Figure 8 shows the microstructure of S31254 and S31254-B alloys with 10%, 20% and 40% deformation strength at 950 °C, respectively. As the deformation increased (Figure 8a–c), the precipitation amount of \(\sigma\) phase in S31254 alloy continuously increased along the austenite grain boundaries. When the deformation reaches 20% (Figure 8b), the precipitates are more concentrated in the grain boundary and become a piece; until the deformation increases to 40% (Figure 8c), the precipitation area of the precipitates is larger and the connection becomes a larger network. Figure 8d–f show the microstructure of different thermal compression deformations corresponding to S31254-B alloys. After adding boron into S31254, the morphology, size, quantity,
distribution and position of the precipitated phase have obviously changed. The precipitated phase in the S31254-B with a 10% and 20% deformation was not reticulated at the grain boundary, as shown in Figure 8d,e. Moreover, when the deformation amount further increased to 40%, the precipitation phase was also not formed to be a large contiguous network. Figure 9 shows the EDS results of the precipitated phase in S31254 and S31254-B with a 20% deformation at 950 °C. The main components of precipitated phase in S31254 were still dominated by high Mo and Cr content, with Mo being 21.68 wt % and Cr being 27.03 wt %. Meanwhile, and the elements in the precipitation of S31254-B alloys also have high Mo and Cr content, with Mo being 22.21 wt % and Cr being 26.57 wt %.

Figure 7. Transmission electron microscope (TEM) bright-field images and corresponding SAED patterns of S31254 samples: (a) matrix (b) precipitates phase.

Figure 8. SEM micrograph of the experimental alloys with different deformation at 950 °C: (a) S31254-10%, (b) S31254-20%, (c) S31254-40%, (d) S31254-B-10%, (e) S31254-B-20%, (f) S31254-B-40%.

Figure 10 shows the XRD pattern of S31254 and S31254-B alloys with 40% hot compression at 950 °C. The diffraction peaks are mainly composed of (111) and (200) planes in this two steels, corresponding to the austenite structure. In addition, the strong diffraction peaks of (100) and (222) planes that is corresponding to σ phase appear in S31254, resulting from the large deformation (40%) at this temperature. Nevertheless, a slight outcrop was found at the (100) plane diffraction peak of σ phase under the same deformation conditions, which further indicates that the addition of boron into S31254 is beneficial to slow down the precipitation of σ phase. Figure 11 shows the microstructures
of S31254 and S31254-B alloys with 40% deformation at 1074 °C. The precipitates of two alloys are mainly distributed in the grain boundaries, but the precipitation amount in S31254-B is less than that in S31254. Figure 12 is the corresponding EDS analysis results of precipitated phase. The Mo and Cr contents of σ phase in both alloys have also no significant change.

**Figure 9.** EDS analysis of the precipitated phase of the experimental alloys with deformation of 20% at 950 °C: (a) S31254, (b) S31254-B.

**Figure 10.** XRD analysis of S31254 and S31254-B alloys with 40% hot compression at 950 °C: (a) S31254, (b) S31254-B.

**Figure 11.** SEM micrograph of the experimental alloys with deformation of 40% at 1074 °C: (a) S31254, (b) S31254-B.
With the increase of deformation amount, the $\sigma$ of steel has been significantly improved, which consequently improved the comprehensive mechanical properties of the content region. Thus, the precipitation position, quantity, size and shape of the precipitation of boron-containing phases at the grain boundary have synergistic effect on the grain strengthening of 304-B steels [27]. Laha K. et al. thought the addition of boron and cerium into 347 stainless steel can inhibit the formation of creep cavity and improve the creep rupture strength [28]. Nakajima H. et al. also found that the boron was helpful for the inhibition of carbides precipitation at the grain boundary of the boron-containing (0.017–0.0019%) 22Mn-13Cr-9Ni-1Mo-0.24N (JK2LB) stainless steel [29].

It has been reported that the addition of trace boron has an important effect on the segregation and precipitation behavior of the grain boundary in steels. Due to the larger difference of atomic radius between the boron and other atoms, the elastic binding energy of boron with other defects, such as dislocations, grain boundaries and vacancy, was also relatively higher, leading to the great driving force of the segregation on the defects locations [26]. The heat-resistance properties of many stainless steels, such as 304, 310, 316, 317 and 347, was enhanced by boron micro-alloying. For example, Yao et al. found that the precipitation of boron-containing phases at the grain boundary and the non-equilibrium segregation of boron at the grain boundary have synergistic effect on the grain strengthening of 304-B steels [27]. Laha K. et al. thought the addition of boron and cerium into 347 stainless steel can inhibit the formation of creep cavity and improve the creep rupture strength [28]. Nakajima H. et al. also found that the boron was helpful for the inhibition of carbides precipitation at the grain boundary of the boron-containing (0.017–0.0019%) 22Mn-13Cr-9Ni-1Mo-0.24N (JK2LB) stainless steel [29].

Therefore, the precipitation behavior in S31254-B steel during the deformation process is speculated and shown in Figure 13b. As the amount of deformation increases, the boron tends to segregate at grain boundaries, forcing the nucleation and growth of $\sigma$ phase in the low boron content region. Thus, the precipitation position, quantity, size and shape of $\sigma$ phase in S31254-B have been significantly improved, which consequently improved the comprehensive mechanical properties of steel.

**Figure 12.** EDS analysis of the precipitated phase in the alloys with 40% deformation at 1074 °C: (a) S31254, (b) S31254-B.
4. Conclusions

The precipitation behavior of σ phase in S31254 and S31254-B alloys has been studied at 950 °C and 1074 °C with different deformation rates, which will be helpful for understanding the influence of boron on the formation of σ phase. The addition of boron into S31254 alloy inhibits the precipitation of σ phase, and improves its precipitation position, shape and distribution. The nose temperature and phase dissolution temperature of σ phase are 950 °C and 1074 °C, respectively. With the increase of deformation magnitude, more σ phase can be found in the microstructure in both alloys, and it will form in the grain boundary first and coarsen to be a network. The addition of boron into the S31254 can inhibit the formation of σ phase, and few σ phases can be found in the S31254-B alloy compared to S31254 alloy under the same deformation conditions.

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