Precipitate Behavior in Fe–20Cr–30Ni–2Nb Austenitic Heat-Resistant Steel

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Abstract In this study, the precipitation behavior of a new austenitic heat-resistant steel (Fe–20Cr–30Ni–2Nb, in at%) was investigated. The effects of alloying addition of boron (B) and lanthanum (La) on the microstructure of the austenitic steel were scrutinized using SEM, EPMA, TEM, and XRD. The results showed that the addition of B enhanced the precipitation of bar-type Laves phase. A small precipitate with high La concentration was observed at the grain boundary in the alloy without aging; similar precipitates without La also presented in region adjacent to the La single phase. This result indicates that La can exist independently and does not contribute to the formation of new compounds. However, in both B- and La-modified alloy, B appeared in the precipitate free zone. In the alloy containing both B and La, only Fe₂Nb Laves-phase precipitates, as indicated by the XRD result.

KEY WORDS: Precipitation free zone; Grain boundary; Phase transformation; Microstructure; Fe–20Cr–30Ni–2Nb austenitic heat-resistant steel

1 Introduction

Coal-fired thermal power plants, operating at high efficiency, are prerequisites for saving resources and energy. Present austenitic steels are capable of operating at temperature higher than 700 °C [1–6]. However, commercial heat-resistant austenitic steels suffer from low creep rupture strengths at such high temperatures. The low creep strength is associated with the carbides/nitrides in

the microstructure, which coarsen during a long-time service [7]. In austenitic stainless steels, carbides at the grain boundaries provide preferential sites for cavity nucleation under creep–fatigue interaction conditions, thereby drastically reducing the creep–fatigue life [2, 8, 9]. Creep strength is the most important mechanical properties at high-temperature services [7]. Takeyama et al. [3] proposed a new type of austenitic heat-resistant steel of Fe–20Cr–30Ni–2Nb (at%), which is strengthened by the thermodynamically stable intermetallic phases of Fe₂Nb TCP (topologically close-packed) phase [3, 10–12]. In the Laves phase, a high thermal stability of Fe₂Nb particle distribution within the γ -Fe matrix was observed in the alloys with small additions of B [3] during creep testing at around 800 °C. La addition is known to refine the grain boundaries in steels, but few researches had focused on the possible effect of La doping to the grain boundaries [13–15].

The objective of this work is to investigate the effect of heat treatment, adding alloy elements such as B and La on the microstructure of Fe–20Cr–30Ni–2Nb.

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2 Experimental

Four alloys of different compositions were prepared, as confirmed by XRF and summarized in Table 1. Alloys were melted from commercially pure metals and drop-casted to make bar ingots with a size of 15 mm × 15 mm × 150 mm. Alloys were cut into pieces of small cubes of 10 mm × 10 mm × 15 mm and homogenized at 1,150 °C for 72 h in vacuum. Then, all the samples were kept at 1,150 °C for 20 min followed by 800 °C for 12 h and quenched in water finally.

Metallographic samples for SEM and EPMA were prepared by grinding the samples using SiC papers until 2000 grit and polishing using 0.1 mm alumina powder and colloidal silica. The as-polished samples were etched in a solution containing 30 mL HCl and 10 mL HNO₃ for 10 s at room temperature. Microstructures of the alloys were examined using a field emission scanning electron microscope (FE-SEM) and transmission electron microscopy (TEM). Phase compositions were analyzed with electron-probe microanalyzer (EPMA). Samples for TEM were prepared by conventional twin-jet electro-polishing using a solution of methanol/perchloric acid with a condition at −20 °C and 60 V for 2 min. Present phases were observed using selected area diffraction patterns (SADP), and phase identification was done by X-ray diffraction (XRD) using CuK_α radiation. Commercial Thermo-Calc software with database SSOL5 was used to calculate the microstructure and identify the possible precipitate phase.

3 Results and Discussion

3.1 Microstructural Evolution

Figure 1 shows the SEM images of the base alloy and alloys with La and B additions. Bar-type and block-type precipitates can be found at the grain boundaries in all alloys. The thickness of bar-type precipitates is approximated as 0.5 μm, and the diagonal of block-type precipitates is 4 μm. Comparing Fig. 1a, b, the addition of B to base alloy increased the line density of precipitation along grain boundary, while doping La did not make large difference about it. Dense generated precipitation in both-modified alloy is also because of boron. Tarigan *et al.* [3] reported that higher density is attributed to better creep rupture strength.

3.2 XRD Analysis

The phase equilibrium of the four alloys at 800 °C was calculated using Thermo-Calc and database SSOL5, and the results are shown in Table 2. In all alloys, γ-phase

Table 1 Compositions of the experimental alloys (wt%)

Alloy	Cr	Ni	Nb	B	La	C	Fe
Base alloy	18.35	31.07	3.28			<0.01	Bal.
B-modified	18.35	31.08	3.28	0.01		<0.01	Bal.
La-modified	18.30	30.98	3.27		0.49	<0.01	Bal.
Both-modified	18.30	30.99	3.27	0.01	0.49	<0.01	Bal.

(austenite) is the largest proportion (>90%) of the present phases. Base alloy and B-modified alloy contained NbNi₃, whereas La-modified alloy showed LaNi₃ phase. Moreover, a small amount of Cr₅B₃ appeared in B-modified alloy, and FeB showed up in alloys modified with both La and B. The calculated phases were confirmed using XRD for four studied alloys although Fe₂Nb is observed in both base alloy and B-modified alloy, as reported elsewhere [3, 16]. Further work is needed to explore this result.

Figure 2 shows the XRD spectrum of the alloys in 2θ range of 34°–49°. Stronger peaks indicate austenite at 43.6°. Moreover, noticeable small peaks represent other remarkable compounds in the microstructure. The results are different from phase calculation using Thermo-Calc: Phases such as NbNi₃ and LaNi₃ FeB did not appear in XRD spectra. Three phases were identified from the smaller peaks: NbC at 34.7° and 40.3° in the base alloy, Fe₃Nb₃C at 37.2°, 44.8°, and Fe₂Nb at 39.1° and 41.6°. No La- or B-based phase was detected by XRD although literature suggests transformation of NbC to Fe₃Nb₃C by B and La additions [17], as shown in Fig. 2 with the disappearance of NbC peak with B and La additions. It has been reported [18] that Fe₃Nb₃C can improve high-temperature strength of ferritic stainless, although the present alloy is austenitic, and henceforth, this is merely a speculation if this phase could increase the alloy strength. The alloy with both La and B additions show only Fe₂Nb peak with austenite peak, and other two peaks remain absent. Fe₂Nb has been reported as to increase the creep strength [3, 10, 11, 16]. Therefore, alloy doped with both B and La is promising alloy with improved mechanical properties at higher temperature service conditions.

3.3 Microstructure and Phase Composition

3.3.1 Fe–20Cr–30Ni–2Nb

Figure 3 shows the element distributions of a precipitate along the grain boundary of Fe–20Cr–30Ni–2Nb alloy. From Fig. 3, it can be concluded that this is a precipitate mainly containing C and Nb. Moreover, the amounts of other elements like Fe, Ni, and Cr in the precipitate are much less than those in matrix.

Fig. 1 SEM images of different alloys after heat treated at 1,150 °C for 20 min and then at 800 °C for 12 h followed water quenching: **a** base alloy; **b** B-modified alloy; **c** La-modified alloy; **d** B and La co-modified alloy

Table 2 Calculated results of the phase amount for different alloys (mol%)

Alloy	fcc matrix	NbNi ₃	LaNi ₃	Cr ₅ B ₃	FeB
Base alloy	92.5	7.41	–	–	–
B-modified	92.6	7.00	–	0.14	–
La-modified	99.1	–	0.80	–	–
Both-modified	99.1	–	0.80	–	0.05

Figure 4 shows the TEM images of the precipitate at the grain boundary of base alloy, Fe₂Nb phase in grain, and its diffraction pattern. Fe₂Nb Laves phase is identified in grain, as indicated by the diffraction pattern. Even though there is no clear diffraction pattern of precipitates at the grain boundary was obtained, the EPMA results (see Fig. 3) suggest this phase should be NbC.

3.3.2 Fe–20Cr–30Ni–2Nb–0.03B

Figure 5 shows the TEM images of the precipitates at the grain boundary of B-modified alloy, Fe₂Nb phase in grain,

Fig. 2 XRD patterns in the 2θ range from 34° to 49° of different alloys: **a** base alloy; **b** B-modified alloy; **c** La-modified alloy; **d** B and La co-modified alloy

Fig. 4 TEM images of the base alloy showing the precipitate on grain boundary **a**; Fe_2Nb phase in grain **b**; diffraction pattern of Fe_2Nb **c**

Fig. 5 TEM images of the B-modified alloy showing the precipitate on grain boundary **a**; Fe_2Nb phase in grain **b**; diffraction pattern of $\text{Nb}_4\text{Ni}_2\text{C}$ **c**

and the diffraction pattern of $\text{Nb}_4\text{Ni}_2\text{C}$. Fe_2Nb in B-modified alloy was generated in grain, and then, it is in line with the result of base alloy. It was reported that the strength increase is obtained by the addition of B into low carbon steel [3, 19]. However, carbon seems to help form other compound like $\text{Nb}_4\text{Ni}_2\text{C}$. It may reduce creep resistance, because M_6C carbide precipitates and coarsens rapidly above 900 °C [20].

3.3.3 $\text{Fe-20Cr-30Ni-2Nb-0.2La}$

Figure 6 shows the EPMA result of La-modified alloy. There is one circle precipitation on grain boundary. It has high La concentration, but La does not exist outside even though bar-type precipitation is above it. Adding La does not affect other

precipitation, contrary to expectation which refines grain boundary [13, 15]. Figure 7 shows the TEM images of precipitation grain boundary in La-modified alloy. $\text{Nb}_4\text{Ni}_2\text{C}$ was observed like it in the B-modified alloy (Fig. 5). The EPMA data show that single La phase does not affect the precipitation on grain boundary, though it facilitates formation of $\text{Nb}_4\text{Ni}_2\text{C}$, which did not appear in the base alloy. B-modified and La-modified alloys have similar XRD peaks, so the addition of alloy elements may affect generating mechanism.

3.3.4 $\text{Fe-20Cr-30Ni-2Nb-0.03B-0.2La}$

Figure 8 shows the EPMA results of precipitation on grain boundary in B and La co-modified alloy after 12-h

Fig. 6 SEM image **a**; EPMA result of La **b** of a precipitate in heat-treated La-modified alloy

Fig. 7 TEM image of a precipitate on grain boundary in La-modified alloy **a**; the diffraction pattern of Nb₄Ni₂C **b**

Fig. 8 SEM image **a**; EPMA results of elements B **b**; Fe **c**; Nb **d** for heat-treated B and La co-modified alloy

aging. It can be found that B appears preferentially in precipitation free zone (PFZ); Fe concentration in matrix is higher than that in the precipitation, while Nb is richer in precipitation. The spots, where B is generated, is noticeable because PFZ often forms in many alloys, suggesting that the nucleation of precipitates is affected to some extent in the vicinity of grain boundaries [21, 22]. This effect should be researched more, in order to check its mechanical property. However, it may result in the formation of a compound except for B on the grain boundary [10]. Figure 9 shows the TEM image and the diffraction pattern of precipitation on grain boundary in B

and La co-modified alloy. From Fig. 9, only Fe₂Nb was observed. As mentioned before, XRD peaks of B and La co-modified alloy indicate austenite and Fe₂Nb. It does not seem that the alloy has other precipitation, which means doping B and La enhances generation of Fe₂Nb on grain boundary, though the mechanism remains unclear.

4 Conclusions

- (1) Two types of precipitates, brock shape and bar shape appeared and increased line density in grain by the

Fig. 9 TEM image of the Fe_2Nb precipitates on grain boundary in B and La co-modified alloy **a**; diffraction pattern of Fe_2Nb **b**

Fig. 3 EPMA results of C, Fe, Ni, Cr, and Nb for a precipitate along the grain boundary in Fe-20Cr-30Ni-2Nb alloy

addition of B into Fe-20Cr-30Ni-2Nb alloy. However, the addition of La did not lead to the increase in line density.

- (2) NbC , $\text{Fe}_3\text{Nb}_3\text{C}$, and Fe_2Nb Laves phases are observed in austenite matrix. NbC was found in base alloy, and the addition of B and La changes NbC to $\text{Fe}_3\text{Nb}_3\text{C}$. Regardless of carbon, only small peaks of Fe_2Nb were observed, except for a peak of matrix in both-modified alloy, which means it may have higher concentration of Fe_2Nb Laves phase.
- (3) Unlike other elements, B appeared in the precipitation free zone, instead of precipitates along grain boundaries. In base alloy, NbC presents on grain boundary, and Fe_2Nb shows up inside grains and on grain boundary. B-modified alloy had $\text{Nb}_4\text{Ni}_2\text{C}$ on grain boundary and Fe_2Nb in grain. La-modified alloy includes La single-phase precipitation on grain boundary. However, La was not contained in other precipitates like bar-shaped ones. Therefore, it exists independently and does not seem to help new precipitates to form.

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