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Impurity Antimony-Induced Creep Property Deterioration and Its Suppression by Rare Earth Cerium for a 9Cr-1Mo Ferritic Heat-Resistant Steel

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Abstract: The high temperature creep properties of three groups of modified 9Cr-1Mo steel samples, undoped, doped with Sb, and doped with Sb and Ce, are evaluated under the applied stresses from 150 MPa to 210 MPa and at the temperatures from 873–923 K. The creep behavior follows the temperature-compensated power law as well as the Monkman-Grant relation. The creep activation energy for the Sb-doped steel (519 kJ/mol) is apparently lower than that for the undoped one (541 kJ/mol), but it is considerably higher for the Sb+Ce-doped steel (621 kJ/mol). Based on the obtained relations, both the creep lifetimes under 50 MPa, 80 MPa, and 100 MPa in the range 853–923 K and the 10^5 h creep rupture strengths at 853 K, 873 K, and 893 K are predicted. It is demonstrated that the creep properties of the Sb-doped steel are considerably deteriorated but those of the Sb+Ce-doped steel are significantly improved as compared with the undoped steel. Microstructural and microchemical characterizations indicate that the minor addition of Ce can stabilize the microstructure of the steel by segregating to grain boundaries and dislocations, thereby offsetting the deleterious effect of Sb by coarsening the microstructure and weakening the grain boundary.

Keywords: heat-resistant steels; creep properties; impurities; rare earths; grain boundaries; segregation

1. Introduction

In recent years, the problems of energy consumption and environmental pollution require advanced power plants with high efficient utilization of fossil energy, which prompts the development of materials for power plants with higher steam temperature and operating pressure. The modified 9Cr-1Mo ferritic heat-resistant steel, i.e., P91 steel, is extensively employed in the power generation and nuclear energy industries owing to its outstanding high temperature mechanical properties that enable higher operating temperatures and pressures to enhance the thermal efficiency [1–3]. Consequently, it is of great significance to explore the creep properties of this steel.

There have been a number of studies concerning the creep properties of the 9Cr steel, most of which focus on the evolution of martensitic microstructures including coarsening of precipitates, decreasing in dislocation density, and growing of martensite lath subgrains. Abe et al. [4] investigated the microstructural instability and its effect on the creep behavior of 9Cr-2W steel and observed that the recovery of dislocations, the agglomeration of carbides, and the growth of martensite lath subgrains occurred during creep with the aid of stress. Spigarelli et al. [5] also found that both large precipitates mainly present on the subgrain boundaries and fine ones mainly present in the subgrain interiors coarsened during creep. Other researchers further found that the creep rupture strength of the high Cr ferritic steel decreased due to the coarsening of precipitates during creep. After a long-term creep

process, a new phase, such as Z-phase, formed at the cost of fine precipitates (MX-type carbides) [6,7]. However, there have been few reports concerning the effect of impurity elements or rare earths on the creep properties of P91 steel. Theoretical calculations indicate that the grain boundary cohesion can be increased by the grain boundary segregation of rare earth elements in iron [8,9], while it can be decreased by the grain boundary segregation of impurity elements, such as tin, phosphorus, and antimony in iron [10]. Our previous studies [11,12] regarding the effects of impurity tin and rare earth cerium on the creep properties of P91 heat-resistant steel demonstrated that tin can significantly deteriorate the creep properties of the steel as it can promote the nucleation of cavities or microcracks by grain or subgrain boundary segregation which weakens the boundary cohesion [11]. However, it is indicated that rare earth cerium can evidently improve the creep properties of the steel due to its segregation to grain or subgrain boundaries [12]. Until the present time, the combined effect of impurity elements and rare earths on the creep properties of P91 steel is little reported.

In the present work, we conducted high-temperature creep tests on the P91 steel samples of three groups: undoped, doped with impurity antimony, and doped with both impurity antimony and rare earth cerium. According to the creep rupture data which were extracted from the creep tests, parameters in the temperature-compensated power law [13] and Monkman-Grant relation [14] were determined. With the two relations above, the creep lifetimes of the steel were predicted at several combinations of stress and temperature within the valid range. After that, microstructural and microchemical observations were carried out so as to explore the effect of impurity antimony and the combined effect of impurity antimony and rare earth cerium on the creep properties of the steel.

2. Materials and Methods

Three heats of P91 steel: undoped, doped with impurity antimony, and doped with both impurity antimony and rare earth cerium, were prepared by vacuum induction melting with 50 kg ingots. The chemical compositions of the steels are listed in Table 1. The ingots were homogenized at 1523 K and then hot rolled in the range of 1273–1373 K into a plate 18 mm in thickness. After being austenitized at 1328 K for 1 h, the steels were air cooled to room temperature, and then tempered at 1033 K for 3 h, followed by water cooling to create a tempered martensite microstructure.

Table 1. Chemical compositions of undoped, Sb-doped, and Sb+Ce-doped steels (wt. %).

Elt.	C	Si	Mn	Sb	Ce	S	P	Cr	Mo	N	Nb	Ni	V	Fe
1	0.12	0.30	0.46	—	—	0.015	0.011	8.85	1.03	0.024	0.075	0.15	0.23	Bal.
2	0.12	0.31	0.47	0.048	—	0.013	0.012	8.95	0.99	0.022	0.071	0.12	0.22	Bal.
3	0.12	0.34	0.46	0.051	0.055	0.011	0.010	9.15	0.97	0.027	0.088	0.16	0.23	Bal.

Note: 1: undoped; 2: Sb-doped; 3: Sb+Ce-doped.

Creep tests were conducted with a high temperature creep testing machine. Since the P91 steel is usually used below 923 K in engineering [15] and the time to rupture is very long if the testing temperature is below 873 K, the creep tests were conducted between 873 K and 923 K. The circular creep specimens with a gage length of 50 mm and a gage diameter of 10 mm were divided into two groups. For one group, the specimens were creep tested at a constant engineering stress of 150 MPa at 873 K, 885 K, 898 K, 910 K and 923 K, respectively, so as to obtain the apparent activation energy (Q_c) for creep in the temperature-compensated power law. For the other group, the tests were conducted at a constant temperature of 873 K under the engineering stresses of 210 MPa, 195 MPa, 180 MPa, 165 MPa, and 150 MPa, respectively, so as to obtain the creep stress exponent (n) in the temperature-compensated power law. At each condition, two specimens were used except testing at a low temperature or stress where one specimen was only employed because the time to rupture was too long.

After creep rupture, to examine the evolution of microstructures and the compositional features at grain or subgrain boundaries, field emission gun scanning transmission electron microscopy equipped with energy dispersive X-ray spectroscopy (FEGSTEM-EDS) was employed. The instrument used in

the present work was JEM-2100F FEGSTEM (JEOL, Tokyo, Japan) equipped with an Oxford INCA energy dispersive X-ray spectrometer (Oxford Instruments, Oxford, UK), operating under a voltage of 200 kV. The disc specimens for FEGSTEM microanalysis were cut from the specimens near the fracture tip as-tempered and creep-tested at 873 K under 150 MPa. More details on FEGSTEM grain boundary microanalysis can be seen in [16,17]. In addition, the morphology of the specimens near the fracture tip was observed using optical microscopy.

3. Results and Discussion

After creep tests, creep data, such as minimum creep rate ($\dot{\epsilon}_m$) and rupture time (t_r), for all three groups of P91 steel specimens were extracted from the creep curves, which are listed in Table A1 (see Appendix A). Based on these data, $\ln(\text{minimum creep rate})$ is plotted as a function of reciprocal temperature ($1/T$) and $\ln(\text{stress})$, as shown in Figure 1a,b, respectively. Clearly, there is a linear relationship between $\ln(\text{minimum creep rate})$ and reciprocal temperature with R -squared values of 0.977, 0.997, and 0.991 (see Figure 1a) or between $\ln(\text{minimum creep rate})$ and $\ln(\text{stress})$ with R -squared values of 0.976, 0.994, and 0.998 (see Figure 1b) for the undoped, Sb-doped, and Sb+Ce-doped steels, respectively. As can be seen, the fitted line for the undoped steel is located under those for the Sb-doped and Sb+Ce-doped steels, showing a better creep behavior. The fitted lines for the Sb-doped and Sb+Ce-doped steels intersect at a certain temperature, indicating that they have different slopes, i.e., different creep activation energy (Q_c) and stress exponent (n) values. Since the lines for the Sb+Ce-doped steel are steeper than those for the Sb-doped one, the former has higher Q_c and n values.

Figure 1. Variation of minimum creep rate with: (a) reciprocal temperature under a stress of 150 MPa; (b) stress at a temperature of 873 K; and (c) rupture time for the undoped, Sb-doped, and Sb+Ce-doped steels.

For the undoped steel, the linear fitting gives:

$$\ln \dot{\epsilon}_m = -65077/T + 64.6 \quad (\sigma = 150 \text{ MPa}) \quad (1)$$

$$\ln \dot{\epsilon}_m = 12.2 \ln \sigma - 70.7 \quad (T = 873 \text{ K}) \quad (2)$$

Experimentally, it is frequently observed that, during the steady-state creep, the strain rate or the minimum creep rate ($\dot{\epsilon}_m$) depends on the applied stress (σ) and exponentially on the absolute temperature (T) in the form of the temperature-compensated power law [13]:

$$\dot{\epsilon}_m = A\sigma^n \exp(-Q_c/RT) \quad (3)$$

where A is a constant, n is the stress exponent for creep, R is the gas constant (8.314 J/mol K), and Q_c is the apparent activation energy for creep. These values are frequently used to estimate the creep properties of steel. The temperature-compensated power law can be rewritten as:

$$\ln \dot{\epsilon}_m = \ln A + n \ln \sigma - Q_c/RT \quad (4)$$

Comparing Equation (4) with Equations (1) and (2), one can obtain $Q_c = 541$ (kJ/mol), $n = 12.1$ and:

$$\ln A + n \ln 150 = 64.6 \quad (5)$$

$$\ln A - Q_c/7258 = -70.7 \quad (6)$$

with Equations (5) and (6), the two values of A may be acquired as $A_1 = 61.2 \text{ h}^{-1}$ and $A_2 = 48.2 \text{ h}^{-1}$. Evidently, these two values are roughly close to each other, implying that there is a fixed value of A in the temperature and stress ranges considered. Hence, the mean value of the two values may be taken as the measured one, i.e., $A = 54.7 \text{ h}^{-1}$. Similarly, for the Sb-doped steel and Sb+Ce-doped steel, one can obtain $Q_c = 519$ (kJ/mol), $n = 11.7$ and $A = 42.7$ (Sb-doped steel), and $Q_c = 621$ (kJ/mol), $n = 13.8$ and $A = 1152.3$ (Sb+Ce-doped steel). Thus, the temperature-compensated power law of creep for the steel may be expressed as:

$$\dot{\epsilon}_m = 54.7\sigma^{12.1} \exp(-541050/RT) \quad (\text{undoped steel}) \quad (7)$$

$$\dot{\epsilon}_m = 42.7\sigma^{11.7} \exp(-519192/RT) \quad (\text{Sb-doped steel}) \quad (8)$$

$$\dot{\epsilon}_m = 1152.3\sigma^{13.8} \exp(-620906/RT) \quad (\text{Sb+Ce-doped steel}) \quad (9)$$

where $\dot{\epsilon}_m$ is in h^{-1} , σ is in MPa, and T is the absolute temperature.

As shown in Equations (7)–(9), the obtained values of stress exponent ($n = 12.1$, $n = 11.7$ and $n = 13.8$ for the undoped, Sb-doped, and Sb+Ce-doped steels, respectively) indicate that all steels deform by the dislocation creep mechanism [18,19]. The acquired values of apparent activation energy ($Q_c = 541$ kJ/mol, $Q_c = 519$ kJ/mol and $Q_c = 621$ kJ/mol for the undoped, Sb-doped, and Sb+Ce-doped steels, respectively) are apparently higher than the activation energy for self-diffusion in iron (close to 240 kJ/mol), which also indicates a dislocation creep mechanism. In addition, the value of Q_c for the undoped steel is apparently higher than that for the Sb-doped one while the values of A and n are close to each other, indicating that at the same temperature and engineering stress the minimum creep rate of the Sb-doped steel is much higher than that of the undoped one. As for the Sb+Ce-doped steel, although the values of A and n are higher than those of the other two steels, the value of Q_c is much higher. This means that, at relatively low temperature and engineering stress where the creep process is mainly dominated by the value of Q_c , the minimum creep rate of the Sb+Ce-doped steel is much lower than that of the other two steels. The changes of stress exponent n and apparent activation energy Q_c in the three steels indicate that the minor additions of Sb and Ce significantly affect the creep process of P91 steel.

As is well known [20], the selection of a material employed at high temperatures needs to take its creep properties into account in engineering design. The creep lifetime of the material under a certain engineering stress or the creep rupture strength of 10^5 h creep lifetime is usually used as a reference.

To estimate the above creep properties of the steel we need to further consider the Monkman-Grant relation, an empirical equation that links the minimum creep rate to the rupture time, which is given by:

$$\dot{\epsilon}_m \times t_r^m = C \quad (10)$$

where $\dot{\epsilon}_m$ is the minimum creep rate, t_r is the rupture time, and m and C are constants. According to the data in Table A1, $\ln(\text{minimum creep rate}, \dot{\epsilon}_m)$ is plotted as a function of $\ln(\text{rupture}, t_r)$ for the three steels in Figure 1c, demonstrating a sound linear relationship with R -square values of 0.997, 0.990; and 0.992, respectively. The linear fitting gives:

$$\ln \dot{\epsilon}_m = -1.06 \ln t_r - 2.70 \quad (\text{undoped steel}) \quad (11)$$

$$\ln \dot{\epsilon}_m = -1.06 \ln t_r - 2.58 \quad (\text{Sb-doped steel}) \quad (12)$$

$$\ln \dot{\epsilon}_m = -1.05 \ln t_r - 2.49 \quad (\text{Sb+Ce-doped steel}) \quad (13)$$

Equation (10) can be rewritten as:

$$\ln \dot{\epsilon}_m = -m \ln t_r + \ln C. \quad (14)$$

with Equations (11)–(14), one can obtain $m = 1.06$ and $C = 0.067$ for the undoped steel, $m = 1.06$ and $C = 0.076$ for the Sb-doped steel, and $m = 1.05$ and $C = 0.083$ for the Sb+Ce-doped steel. As a consequence, there are:

$$\dot{\epsilon}_m \times t_r^{1.06} = 0.067 \quad (\text{undoped steel}) \quad (15)$$

$$\dot{\epsilon}_m \times t_r^{1.06} = 0.076 \quad (\text{Sb-undoped steel}) \quad (16)$$

$$\dot{\epsilon}_m \times t_r^{1.05} = 0.083 \quad (\text{Sb+Ce-undoped steel}) \quad (17)$$

where $\dot{\epsilon}_m$ is in h^{-1} and t_r is in h.

As seen, the values of parameter m or C are very close to each other for the three steels, indicating that impurity Sb or rare earth Ce does not influence the Monkman-Grant relation of the material. Using Equations (7)–(9) along with Equations (15)–(17), one can estimate the creep lifetime at any temperature under any stress with the assumption that both the temperature-compensated power law and the Monkman-Grant equations are valid under the temperature and stress conditions considered. Owing to the fact that the P91 steel is usually employed at a temperature below 923 K and at a stress below 100 MPa in engineering [15], we estimate the 50 MPa, 80 MPa, and 100 MPa stress creep lifetimes at temperatures between 853 K and 923 K, and the creep rupture strengths of 10^5 h creep lifetime at 853 K, 873 K, and 893 K, respectively. The estimated results are shown in Figure 2. Obviously, the 100 MPa stress creep lifetime for the Sb-doped steel is much shorter (up to fifty percent shorter) than that for the undoped steel in the range 853–923 K, while the 100 MPa stress creep lifetime for the Sb+Ce-doped steel is close to that for the undoped steel in the range 893–923 K. However, in the range 853–893 K where the P91 steel is usually employed in engineering, the 100 MPa stress creep lifetime for the Sb+Ce-doped steel is apparently longer (1.1 to 1.8 times longer) than that for the undoped steel. Similarly, under 80 MPa and 50 MPa which are closer to the service stress of the P91 steel, the creep lifetime for the Sb-doped steel is much shorter (about fifty percent shorter) than that for the undoped-steel (see Figure 2b,c), indicating that the creep properties of the Sb-doped steel worsen significantly due to the effect of impurity Sb. As for the Sb+Ce-doped steel under the above condition, the creep lifetime is much longer (about 10 times longer) than that for the undoped steel (see Figure 2b,c), implying that the creep properties of the steel are significantly improved due to the effect of rare earth Ce. The estimates of the creep rupture strength of 10^5 h creep lifetime at 853 K, 873 K, and 893 K also show that the creep rupture strength for the Sb-doped steel is about 7% lower than that for the undoped steel, but it is about 3% higher for the Sb+Ce-doped steel (see Figure 2d).

Figure 2. (a) 100 MPa-stress creep lifetime; (b) 80 MPa-stress creep lifetime; (c) 50 MPa-stress creep lifetime; and (d) 10^5 h creep rupture strength of the steels at 853 K, 873 K, and 893 K for the undoped, Sb-doped, and Sb+Ce-doped steels.

The evolution of the microstructure of P91 steel plays a crucial role in the creep processes of the material. Normally, during creep, microstructure coarsening, such as precipitate coarsening, dislocation density decrease, and subgrain disappearance, occurs, which deteriorates the creep properties of the steel. In order to explore the effect of impurity Sb and rare earth Ce on the microstructure evolution, TEM micrographs were taken from the as-tempered specimens, as well as the specimens crept at 873 K under 150 MPa for the three steels, which are shown in Figure 3. As seen, the as-tempered specimens (Figure 3a,c,e) exhibit a typical tempered martensite microstructure. The microstructure is with a high density of dislocations and precipitates shown as black dots, which are distributed along prior austenite grain boundaries or martensite lath boundaries. It is indicated by EDS microanalysis that there are two types of precipitates: coarser ones with sizes ranging from 100 nm to 200 nm, which mainly contain Cr, and finer ones with sizes less than 100 nm, which mainly contain Nb and V. Accordingly, the coarser precipitates, such as those marked by square in Figure 3, could be $M_{23}C_6$ -type carbides and the finer ones, such as those marked by circle in Figure 3, could be MX-type carbides [6]. The precipitates in the undoped (Figure 3a) and Sb+Ce-doped steels (Figure 3e) are a little more than those in the Sb-doped steel (Figure 3c) and their dislocation density are somewhat higher. As shown in Figure 3b,d,f, the dislocation density is reduced apparently and the precipitates as well as the martensite laths are coarsened after the creep test. However, there are still some dislocations and subgrains remaining in the undoped and Sb+Ce-doped steels after the creep test, but there are almost no dislocations or subgrains remaining in the Sb-doped steel. This means that the degradation in microstructure is accelerated due to impurity Sb in the creep process, while rare earth Ce can stabilize the microstructure, thus significantly offsetting the detrimental effect of impurity Sb.

Figure 3. Transmission electron micrographs of the specimens as-tempered and creep-tested under 150 MPa at 873 K (the coarser precipitates, such as those marked by a square, are $M_{23}C_6$ -type, while the finer ones, such as those marked by a circle are MX-type): (a) undoped steel as tempered; (b) undoped steel after creep test; (c) Sb-doped steel as tempered; (d) Sb-doped steel after creep test; (e) Sb+Ce-doped steel as tempered; and (f) Sb+Ce-doped steel after creep test.

Creep rupture is also related to the voids that nucleate, grow and cluster during creep. Study by Otto et al. [21] indicates that the small addition of impurity elements significantly deteriorates the creep properties in Cu-0.008 wt. % Bi and Cu-0.092 wt. % Sb, which is associated with the promotion of the formation of intergranular creep damage such as cavities and microcracks by Bi and Sb. Therefore, we observed the morphology of voids near the fracture tip for the three kinds of specimens tested at 873 K under 150 MPa, which are shown in Figure 4. As can be seen, the voids in the Sb-doped specimens (see Figure 4b) are much more than those in the undoped (see Figure 4a) and Sb+Ce-doped specimens (see Figure 4c) where the void morphology is similar to each other. Accordingly, Sb can

promote the nucleation of voids while the nucleation of voids is restrained in the Sb+Ce-doped steel. It may be claimed that the promoted formation of voids in the Sb-doped steel may deteriorate its creep properties and thus accelerate creep rupture while the minor addition of Ce can suppress the effect of Sb, thereby improving the creep properties. In addition, as shown in Figure 4b, many voids in the Sb-doped steel have linked together and formed linear cracks parallel to the applied stress. With consideration of the deformation texture of the specimens near the fracture tip where the grains are elongated along the direction of the applied stress unless recrystallization takes place, it can be envisaged that the voids are initiated from the boundaries parallel to the applied stress. This is reasonable because during creep the vacancies migrate from the boundaries perpendicular to the applied stress to those parallel to the applied stress. It may be stated from the aforementioned results that the enhancement of void formation in the Sb-doped specimen may be related to the Sb boundary segregation, while the significant decrease of voids in the Sb+Ce-doped specimen may be related to the effect of Ce boundary segregation.

Figure 4. Morphology of voids near the fracture tip in the specimens tested under 150 MPa at 873 K: (a) undoped steel ruptured after 1010 h; (b) Sb-doped steel ruptured after 423 h; (c) Sb+Ce-doped steel ruptured after 601 h.

During creep, both impurity element tin and rare earth element cerium can segregate to the grain or subgrain boundaries [22,23]. The equilibrium segregation may occur during isothermal holding prior to creep loading and the non-equilibrium segregation may take place during creep, which is related to a vacancy-solute complex effect or boundary diffusion effect [24,25]. The segregation of impurity element can reduce considerably the grain boundary cohesion in steel, thus promoting the nucleation of cavities on the grain boundaries [10,21] and deteriorating the creep properties of the steel. Nevertheless, the rare earth element can increase the grain boundary cohesion in steel, thus improving the creep properties of the steel. To explore the segregation behavior in the Sb-doped and Sb+Ce-doped specimens, the concentrations of Sb and Ce at the boundaries were measured with the use of FEGSTEM after the specimens were tempered and creep-tested at 873 K under 150 MPa. Figure 5 represents an FEGSTEM image showing a segment of grain boundary analyzed, which is free from precipitates. Moreover, the boundary is quite parallel to the incident electron beam, which is suitable for FEGSTEM

boundary microanalysis. The boundary concentrations of Sb and Ce are given in Figure 6 with its matrix concentration plotted for comparison. Obviously, both impurity Sb and rare earth Ce segregate apparently to the boundaries in the specimens as tempered or creep-tested. The boundary levels of both Sb and Ce are over 20 times higher than their matrix levels. The average boundary concentration of Sb in the Sb-doped specimen increases by approximately 40% after creep-tested (from 0.47 at. % to 0.64 at. %, see Figure 6a,c), while the average boundary concentration of Sb in the Sb+Ce-doped specimen as tempered (0.53 at. %) is almost the same as that in the Sb+Ce-doped specimen creep-tested (0.58 at. %). For clarity, the average boundary concentrations of Sb in the Sb-doped and Sb+Ce-doped specimens as tempered and creep-tested are represented in Figure 7.

Figure 5. FEGSTEM image showing a segment of grain boundary analyzed.

Figure 6. (a) Grain boundary concentration of Sb in the Sb-doped specimen as tempered; (b) grain boundary concentrations of Sb and Ce in the Sb+Ce-doped specimen as tempered; (c) grain boundary concentration of Sb in the Sb-doped specimen creep-tested under 150 MPa at 873 K (the specimen ruptured after 423 h); and (d) grain boundary concentrations of Sb and Ce in the Sb+Ce-doped specimen creep-tested under 150 MPa at 873 K (the specimen ruptured after 601 h), with the matrix concentration plotted for comparison (the error bar represents the standard deviation).

Figure 7. Grain boundary concentrations of Sb in the Sb-doped and Sb+Ce-doped specimens as tempered and creep tested (the Sb-doped specimen ruptured after 423 h and the Sb+Ce-doped specimen ruptured after 601 h. The error bar represents the standard deviation).

As discussed above, the boundary cohesion can be considerably increased by the boundary segregation of Ce, which can compensate the detrimental effect of Sb and thereby restrain the initiation of cavities and microcracks. In other words, rare earth Ce can strengthen the boundary in steel. Moreover, rare earth Ce could also segregate to dislocations, which may restrict the slip and climb of the dislocations, thus stabilizing the dislocations and leading to a higher apparent activation energy for creep (621 kJ/mol). With these mechanisms, rare earth Ce can stabilize the microstructure of the steel during creep, which may be the reason why there are more dislocations and subgrains remaining in the Sb+Ce-doped specimen than in the Sb-doped specimen after creep test, and the microstructure in the Sb+Ce-doped specimen are not apparently coarsened as compared with that in the Sb-doped specimen. In addition, as shown in Figure 7, the rare earth Ce in the Sb+Ce-doped steel can reduce the boundary segregation of Sb, thus suppressing the effect of Sb to a certain degree. Consequently, the creep properties of the Sb+Ce-doped steel are apparently better than those of the Sb-doped steel.

4. Conclusions

The creep properties of three groups of P91 ferritic heat-resistant steel specimens, undoped, doped with antimony, and doped with both antimony and cerium, are examined under the applied stresses from 150–210 MPa and at the temperatures from 873–923 K. The creep behaviors agree with the temperature-compensated power law and Monkman–Grant relation. For the temperature-compensated power law equation, the values of apparent activation energy and stress exponent for creep are about 541 kJ/mol and 12.1 for the undoped steel, 519 kJ/mol, and 11.7 for the Sb-doped steel, and 621 kJ/mol and 13.8 for the Sb+Ce-doped steel, respectively. For the Monkman–Grant equation, the values of constants m and C are around 1.06 and 0.067 for the undoped steel, 1.06 and 0.076 for the Sb-doped steel, and 1.05 and 0.083 for the Sb+Ce-doped steel, respectively. In terms of these relationships, the creep lifetimes for the three steels are predicted under several conditions. It is demonstrated that minor Sb can significantly deteriorate the creep properties of the steel, but they can, evidently, be improved by the minor addition of Ce. Rare earth Ce can both strengthen the grain boundary and stabilize the microstructure of the steel by segregating to grain boundaries and dislocations, which leads to a high apparent activation energy for creep (621 kJ/mol). This beneficial effect can offset the detrimental effect of Sb that enhances the coarsening of microstructure and deteriorates the grain boundary by segregation.

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Appendix A

After creep tests, the values of minimum creep rate and creep rupture time were obtained from the creep curves. These data are listed in Table A1.

Table A1. Minimum creep rate and rupture time for the undoped, Sb-doped, and Sb+Ce-doped specimens tested at various engineering stresses and temperatures.

Temp. (K)	Stress (MPa)	Creep Rate (h^{-1})			Rupture Time (h)		
		Undoped	Sb-Doped	Sb+Ce-Doped	Undoped	Sb-Doped	Sb+Ce-Doped
923	150 (test 1)	1.98×10^{-3}	5.27×10^{-3}	8.37×10^{-3}	26	10	8.4
923	150 (test 2)	2.90×10^{-3}	6.13×10^{-3}	8.59×10^{-3}	18	9.5	8.8
910	150 (test 1)	1.31×10^{-3}	2.24×10^{-3}	3.52×10^{-3}	39	30	21
910	150 (test 2)	1.15×10^{-3}	2.01×10^{-3}	3.33×10^{-3}	47	34	24
898	150 (test 1)	3.74×10^{-4}	8.13×10^{-4}	1.18×10^{-3}	131	71	56
898	150 (test 2)	4.70×10^{-4}	8.53×10^{-4}	8.77×10^{-4}	101	66	70
885	150 (test 1)	1.42×10^{-4}	2.86×10^{-4}	2.87×10^{-4}	347	175	210
873	150 (test 1)	4.20×10^{-5}	1.25×10^{-4}	8.60×10^{-5}	1010	423	601
873	165 (test 1)	8.60×10^{-5}	2.82×10^{-4}	2.97×10^{-4}	507	177	220
873	180 (test 1)	4.02×10^{-4}	8.80×10^{-4}	1.08×10^{-3}	126	72	82
873	180 (test 2)	4.64×10^{-4}	9.87×10^{-4}	9.94×10^{-4}	120	66	85
873	195 (test 1)	9.58×10^{-4}	2.51×10^{-3}	2.74×10^{-3}	58	29	25
873	195 (test 2)	7.62×10^{-4}	2.22×10^{-3}	3.21×10^{-3}	70	33	20
873	210 (test 1)	2.47×10^{-3}	6.01×10^{-3}	8.77×10^{-3}	24	11	8.2
873	210 (test 2)	1.99×10^{-3}	5.67×10^{-3}	8.96×10^{-3}	28	12	8.1

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