Dependence of Precipitation Behavior and Creep Strength on Cr Content in High Cr Ferritic Heat Resistant Steels*

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Abstract

It is known that high temperature tensile strength increases with increasing Cr content in Cr containing heat resistant steels. Recently, however, it was found that long-term creep strength decreased with increasing Cr content in the heat resistant steels containing 8.5-12%Cr. In this study, precipitation behavior of $M_{23}C_6$ carbide and the Z phase after creep tests was investigated using two kinds of high Cr ferritic steels (9Cr and 10.5Cr). As a result, 10.5Cr steel exhibited larger average particle size of $M_{23}C_6$ than 9Cr steel irrespective of creep stress levels, but the amount of $M_{23}C_6$ carbide was almost the same in both steels. On the other hand, the amount of the Z phase became large in 10.5Cr steel compared with 9Cr steel. These experimental results indicate that high level of Cr content accelerates precipitation and coalescence rate of both $M_{23}C_6$ carbide and the Z phase, resulting in degradation of long term creep strength in 10.5 Cr steel compared to 9Cr steel.

Key words: Precipitation, $M_{23}C_6$ Carbide, Z Phase, Long Term Creep, High Cr, Ferritic Steel

1. Introduction

It is known that high Cr heat resistant ferritic steels show the premature failure in creep rupture at 650°C, i.e., the creep strength in a long time becomes lower than the expected values extrapolated from short time creep tests ⁽¹⁾. Recently, the dependence of this premature failure on Cr content in high Cr (8.5-12%Cr) ferritic steels has been investigated systematically and was reported that the rupture strength in the long time over 10000h increased with decreasing Cr content in those high Cr ferritic steels ^(2,3). As a result, 8.5%Cr steel shows never premature failure even at 650°C. The mechanism of the trade-off relationship between high temperature tensile strength and creep strength with respect to Cr content is still unknown.

In general, the long term creep strength of high Cr ferritic steels is known to be related

closely to the microstructural evolution of them. The purpose of this study is to investigate microstructural evolution after creep tests in high Cr ferritic steels varying only the Cr content. In particular, this investigation is focused on the precipitation and coalescence behavior of $M_{23}C_6$ carbide and the Z phase, both of which contain a large amount of Cr.

2. Experimental Procedure

Two kinds of steels varying only Cr content are used in this study. Their chemical compositions are listed in Table 1. Except for Cr, all elements are similar to each other within an error, and these two steels contain 0.1C, 3Co, 3.5W, V, Nb, Mo, B and N. Cr contents of these steels are 9.0% and 10.5%. Hereafter, they are called as 9Cr steel and 10.5Cr steel, respectively. A typical result on creep rupture tests reported so far in both steels is shown in Fig.1^(2,3), and it was found that 10.5Cr steel showed a premature failure at 650°C in a long time compared to 9Cr steel.

Table 1 Chemical compositions of the experimental steels used. (mass%)

Steel	C	Si	Mn	Ni	Cr	Mo	V	Nb	W	Co	B	N
9Cr Steel	0.09	0.03	0.01	0.21	9.0	0.11	0.15	0.06	3.6	3.0	0.009	0.020
10.5Cr Steel	0.10	0.03	0.01	0.20	10.5	0.10	0.15	0.06	3.5	3.0	0.010	0.021

Fig.1 Time to rupture curves of 9Cr and 10.5Cr steels at 650°C

Extraction replicas were prepared from the steels crept or simple aged specimens at 650°C. Precipitates on the replica were analyzed with STEM/EDX and were classified as MX carbonitride, $M_{23}C_6$ carbide, the Laves phase or the Z phase on the basis of the amounts of Cr, V, Nb, W and Fe in each precipitate, i.e., almost all metallic element in MX carbonitride is V or Nb, $M_{23}C_6$ carbide is Cr, whereas the Laves phase shows $(Fe,Cr)_2W$ type concentration ratio and the Z phase contains both Cr and V⁽⁴⁾, as mentioned below.

On the basis of STEM/EDX data taken from a series of the specimens, the sizes of $M_{23}C_6$ carbide and the Z phase were obtained by means of image analysis and also the volume fraction of them was measured with the area analyzing method⁽⁵⁾. From these measured data, change in the size with annealing time was obtained.

3. Experimental Results and Discussion

TEM microstructures of 9Cr and 10.5Cr steels as tempered state are shown in Fig.2. The both microstructures are almost the same and show the lath martensite structure containing fine precipitates of the Laves phase⁽⁶⁾ together with granular $M_{23}C_6$ carbide. In crept specimens, besides these precipitates, the Z phase was observed. Typical EDX data taken from $M_{23}C_6$ carbide and the Z phase is shown in Fig.3. $M_{23}C_6$ carbide consists mainly of Cr and contains Fe together with a small amount of Mo and W, whereas the Z phase contains about 50%Cr, 20%V and several % of Nb. Thus, the Z phase can be distinguished from $M_{23}C_6$ carbide and the Laves phase ($Fe_2(Mo,W)$). Volume fractions of $M_{23}C_6$ carbide and the Z phase in 9Cr and 10.5Cr steels annealed at 650°C without stress (grip portion of the crept specimens) are shown in Fig.4. In this figure, the equilibrium volume fraction of each phase, which is calculated by using the Thermo-Calc, is also shown as an arrow in the right hand side. It is found that the amount of $M_{23}C_6$ carbide exhibits a constant level irrespective to the annealing time and it is almost the same as the equilibrium value in each steel. This fact indicates that $M_{23}C_6$ carbide becomes nearly the equilibrium state even in the tempered state.

Fig.2 TEM microstructures of 9Cr and 10.5Cr steels as tempered state

Fig.3 Typical EDX data taken from $M_{23}C_6$ carbide and the Z phase on the extraction replica

The Z phase is observed remarkably in 10.5Cr steel annealed over 5000h but is scarcely observed in 9Cr steel, in which the Z phase is found a little after more than 25000h annealing, as shown in open square marks in Fig.4. The amount of the Z phase becomes a constant value in 10.5Cr steel after 10000h annealing and this value is similar to the calculated equilibrium one, whereas the amount of the Z phase in 9Cr steel after 30000h annealing is still lower than the equilibrium value. These results are direct evidence that the Z phase form easily in high Cr steels compared to low Cr steels.

Fig.4 Volume fractions of $M_{23}C_6$ carbide and the Z phase in 9Cr and 10.5Cr steels annealed at 650°C without stress

Fig.5 Volume fraction of the Z-phase obtained from the gauge parts of 9Cr and 10.5Cr steels both after creep tests at 650°C.

Figure 5 shows a plot of the volume fraction of the Z phase obtained from the gauge portion in crept specimens of 9Cr and 10.5Cr steels against the rupture time (corresponding to the annealing time) at 650°C with several stress levels. In the gauge portion, trend of

the Z phase precipitation is similar to that in the grip parts, i.e., 10.5Cr steels shows much larger amount of the Z phase than 9Cr steel. Here, it can be observed that the volume fraction of the Z phase depends on stress levels and it becomes high in the specimen undergone high stress condition irrespective of Cr content in the steels. This fact indicates that creep stress accelerates the Z phase formation in high Cr ferritic steels.

Fig.6 Change in the radius of both $M_{23}C_6$ carbide and the Z-phase with annealing time in both 9Cr and 10.5Cr steels annealed at 650°C

Figure 6 shows the change in radius of both $M_{23}C_6$ carbide and the Z phase with annealing time in both 9Cr and 10.5Cr steels annealed at 650°C without any stress. Straight lines in this figure are obtained from the regression analysis using the data corresponding to the constant volume fractions of both $M_{23}C_6$ carbide and the Z phase, as shown in Fig.4. Thus the data on the Z phase obtained in 10.5Cr steel annealed for 5000h is omitted from the regression analysis. The coalescence rate of $M_{23}C_6$ carbide exhibits no difference between the two steels and it depends on $t^{1/3}$ of annealing time, indicating that the rate controlling process of $M_{23}C_6$ carbide is atomic diffusion. Although the coalescence rate is the same in the two steels, the size of $M_{23}C_6$ carbide in 10.5Cr steel is much larger than that in 9Cr steel. For example, the size is about 73 and 100 μm at $1 \times 10^4 h$ and $3 \times 10^4 h$, respectively, in 10.5Cr steel and about 60 and 80 μm at $1.3 \times 10^4 h$ and $3 \times 10^4 h$, respectively, in 9Cr steel. Since the size as tempered state r_0 is almost the same in both steels as can be seen in Fig.6, the size difference in the two steels after annealing is attributable to the difference in the rate constant k as the following equation.

$$r - r_0 = kt^{1/3}$$

On the other hand, the dependence of the Z phase size on annealing time is quite different from that of $M_{23}C_6$ carbide, although the data is only obtained from 10.5Cr steel, in which the Z phase is observed relatively in the early stage of annealing. As shown in Fig.6, the coalescence rate of the Z phase depends on $t^{1/2}$ of annealing time, indicating that the Z-phase coagulates much faster than $M_{23}C_6$ carbide and that the rate controlling process is interface reaction (interfacial moving). As a result, the size of the Z-phase in 10.5Cr steel is about 60 μm at $1 \times 10^4 h$, the value of which is much smaller than 73 μm of $M_{23}C_6$ carbide at the same annealing time, but it becomes about 110 μm at $3 \times 10^4 h$. This is much larger than that of $M_{23}C_6$ carbide.

Figure 7 shows TEM microstructures taken from the two steels crept at 650°C for 2731h in 10.5Cr steel and for 5289h in 9Cr steel. Comparing the two microstructures, it is obvious that the progress of microstructural evolution in 10.5Cr is faster than that in 9Cr steel, even though the crept time of 9Cr steel is about two times longer than that of 10.5Cr steel.

Fig.7 TEM microstructures after 650°C creep rupture tests. Rupture times and the stress levels are 5289h at 157MPa in 9Cr steel and 2731h at 118MPa in 10.5Cr steel, respectively.

It has been believed that the premature failure occurring in high Cr heat resistant ferritic steels is due to replacing the fine MX carbonitride by the coarse Z phase during creep at high temperatures. Also, it is reported that thermodynamic potential for the Z phase formation increase with increasing Cr content in high Cr ferritic steels ⁽⁷⁾, resulting in occurring the Z phase formation easily in high Cr steels. This is consistent with the results obtained in this study. However, the Z phase formed in the early stage is not so large size, as shown in Fig.6. Furthermore, the size of $M_{23}C_6$ carbide depends on Cr content in the steels, i.e., it is smaller in 9Cr steel than that in 10.5Cr steel. These facts indicate that not only the Z phase formation but also the difference in the coalescence rate of $M_{23}C_6$ carbide between the two steels affects the long term creep strength of the steels. This microstructural difference appears in a long term, and hence it is considered that Cr diffusivity should be changed by Cr content in steels, because atomic diffusivity affects the behavior of all precipitates and microstructural evolution. In fact, it is reported that the interdiffusion coefficient becomes lower with increasing up to 12mass%Cr in Fe-Cr binary system ⁽⁸⁾. This difference of diffusivity depending on Cr content in steels affects every process related to diffusion process in the steels, resulting in the difference in the microstructural evolution between 9Cr steel and 10.5Cr steel.

4. Summary

In order to make clear the premature failure observed in creep of high Cr heat resistant steels, the precipitation behavior at 650°C of both $M_{23}C_6$ carbide and the Z phase was investigated using two kinds of high Cr heat resistant steels varying only Cr content. The results are summarized as follows.

- (1) The amount of $M_{23}C_6$ carbide is almost the same in the two steels, but the Z phase amount in 10.5Cr steel in annealed specimens is larger than that in 9Cr steel.
- (2) It is observed that the size of $M_{23}C_6$ carbide in 9.0Cr steel is much smaller than that in

10.5Cr steel.

(3) The coalescence rate of $M_{23}C_6$ carbide is found to be proportional to $t^{1/3}$ in both steels, indicating that the rate controlling process for the coalescence of $M_{23}C_6$ carbide is diffusion.

(4) The coalescence rate of the Z phase measured in the 10.5Cr steel is proportional to $t^{1/2}$, implying that the rate controlling process for the coalescence of the Z phase is interfacial reaction (interfacial moving).

(5) These phenomena mentioned above are considered to be one of the reasons for the premature failure observed in 10.5Cr steel in a long term creep test.

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