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Study on the nucleation and growth of $M_{23}C_6$ carbides in a 10% Cr martensite ferritic steel after long-term aging

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In the 10% Cr martensite ferritic steel, it is found that most of $M_{23}C_6$ carbides appear on high angle boundaries (HABs) with a misorientation angle of 40°–60° and only a small amount of them precipitate at low angle boundaries (LABs) with a misorientation angle of 8°–15°. It has always been considered that V is added to mainly form MX carbides. However, in the present work, V will also diffuse into $M_{23}C_6$ carbides after aged at 650 °C for 12,000 h, which not only replaces Fe but also W and Mo. From the initial state to 25,000 h, the variation of the mean size of $M_{23}C_6$ basically obeys the Lifshitz–Slyozov–Wagner coarsening theory. When the V content in $M_{23}C_6$ gradually increases from 12,000 h to 25,000 h, the coarsening rate of $M_{23}C_6$ decreases remarkably. The V in $M_{23}C_6$ plays an important role in controlling the coarsening of $M_{23}C_6$ carbides in this stage.

1. Introduction

9–12% Cr tempered martensite ferritic steels are important high-temperature materials which are used for critical components of fossil-fired power plants operated in the creep range at temperatures between 773 and 923 K [1–3]. These steels generally consist of tempered martensite matrix, precipitates of MX carbonitrides, $M_{23}C_6$ carbides, and intermetallic compounds such as Laves phase and z phase [4].

In the 9–12% Cr martensite ferritic steel, it is well known that subgrain stability is a decisive factor for the creep strength [5–8]. Maruyama et al. [9] found that $M_{23}C_6$ precipitates play a more important role than MX precipitates in the control of the subgrain coarsening, which is mainly because the $M_{23}C_6$ particles are in a similar size to the thickness of subgrain boundaries during long-term static aging or creep. The stabilization of subgrain boundaries is mainly due to the presence of small $M_{23}C_6$ particles close to the boundaries, where they exert Zener forces [6]. However, $M_{23}C_6$ carbides tend to coarsen easily during creep because they contain iron and chromium, which are major constituents of $M_{23}C_6$, is large [10]. Hence, it is very important to prevent the growth of $M_{23}C_6$ carbides for improving the creep strength.

The growth and coarsening of $M_{23}C_6$ carbides are controlled by the diffusion of the substitutional components [11–12]. It has been reported that Co and B can decrease the coarsening rate of $M_{23}C_6$ carbides in 9–12% Cr martensite ferritic steel [13–14]. From a different point of view, Abe [15] systematically investigated on the coarsening of $M_{23}C_6$ particles in Fe–9Cr–W steels as a function of the tungsten content and of time during creep testing at 600 °C, and proved that the addition of tungsten reduces the coarsening rate of $M_{23}C_6$ carbides. Based on Abe's results, Bhadeshia [16] and Ghosh [17] carried out the corresponding research and proposed different explanations, which seem more reasonable because they took into account all of the phases that are present.

It is well known that the substitutional alloying elements, such as Cr, Mo, V and Mn, replace Fe in carbides as thermal exposure time increases [12,18]. Aghajani et al. [1] studied the evolution of the microstructure of a 12% Cr tempered martensite ferritic steel during long-term aging and creep, and found that Cr and Mo content increases up to 51,072 h (creep exposure) at the expense of Fe content in $M_{23}C_6$ carbides.

In the 10% Cr tempered martensite ferritic steel, $M_{23}C_6$ carbides are mainly composed of Fe, C, Cr, Mo and W [19]. The aim of the present study is to research the precipitation and growth behavior of $M_{23}C_6$ carbides in the 10% Cr martensite ferritic steel during long-term aging, focusing on the variations of chemical composition and size of $M_{23}C_6$ carbides and trying to establish the correlation between them.

2. Materials and experimental methods

The chemical composition of the 10% Cr martensite ferritic steel is listed in Table 1. The material was austenitized at 1050 °C for 21.5 h

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Table 1
Chemical composition (wt.%) of the 10% Cr steel.

Element	C	Si	Mn	P	S	Cr	Ni	Mo	V	Nb	W	N
wt.%	0.13	0.06	0.42	0.012	0.003	10.46	0.76	1.01	0.19	0.05	1.04	0.06

and then cooled in oil, followed by tempering at 570 °C for 21 h in the first step and at 690 °C for 23 h in the second step. Subsequently, long-term aging experiments were performed at 650 °C for 1000 h, 4000 h, 6000 h, 12,000 h, 18,000 h, 21,000 h, 23,000 h and 25,000 h, respectively.

The detailed microstructure of precipitates were examined by transmission electron microscope (TEM JSM-2010), thin foils for TEM were prepared by double jet electro-polishing using a 7% solution of perchloric acid in glacial acetic acid. In order to reveal the effect of grain boundary misorientation on precipitation behavior of $M_{23}C_6$ carbides, electron back-scattered diffraction (EBSD) measurements were performed using a scanning electron microscope (SEM S3400N). The samples for the EBSD analysis were first ground up to 2000 grit and then polished with diamond paste to 1 μm and final further polishing with a 0.04 μm colloidal silica suspension for 2 h. The orientation maps were measured by EBSD at an accelerating voltage of 20 KV and a step size of 100 nm.

3. Results and discussion

3.1. Effect of the grain boundary misorientation on the precipitation behavior of $M_{23}C_6$ carbides

All EBSD orientation maps were obtained from the specimens aged at 650 °C for 4000 h. It can be seen from Fig. 1(b) that one $M_{23}C_6$ carbide precipitated at grain boundaries with a misorientation angle of 59°, the other one precipitated at grain boundaries with a misorientation angle of 13.5°. A total of 80 particles of $M_{23}C_6$ were analyzed, statistical data shows that most of $M_{23}C_6$ carbides appear on high angle boundaries (HABs) with a misorientation angle of 40°–60° and only a small amount of them precipitate at low angle boundaries (LABs) with a misorientation angle of 8°–15°.

Tang et al. [20] and Richard et al. [21] have confirmed that CSL boundaries and the grain boundaries with low misorientation angle are immune to precipitation. They have explained that the low-angle and CSL boundaries have relatively higher degree of atomic matching, which would lead to lower grain boundary energy in comparison with the random high-angle grain boundaries. Their discussion on the relation between precipitation and grain boundary characteristic could also be used to explain the precipitation behavior of $M_{23}C_6$ carbides in this research.

3.2. Nucleation and growth behavior for $M_{23}C_6$ carbides

Fig. 2 shows a bright field image, the corresponding SAED patterns and EDS results of the specimens in initial condition, aged at 650 °C for 12,000 h and for 25,000 h, respectively. From Fig. 2(a), it is noted that $M_{23}C_6$ carbides locate at martensite lath boundaries, and have short rod-like shape. Analysis of the SAED patterns indicates that $M_{23}C_6$ is a face-centered cubic structure, and the EDS results shows that $M_{23}C_6$ consists of Fe, C, Cr, Mo and W, which is in agreement with the previous studies [4,22–24].

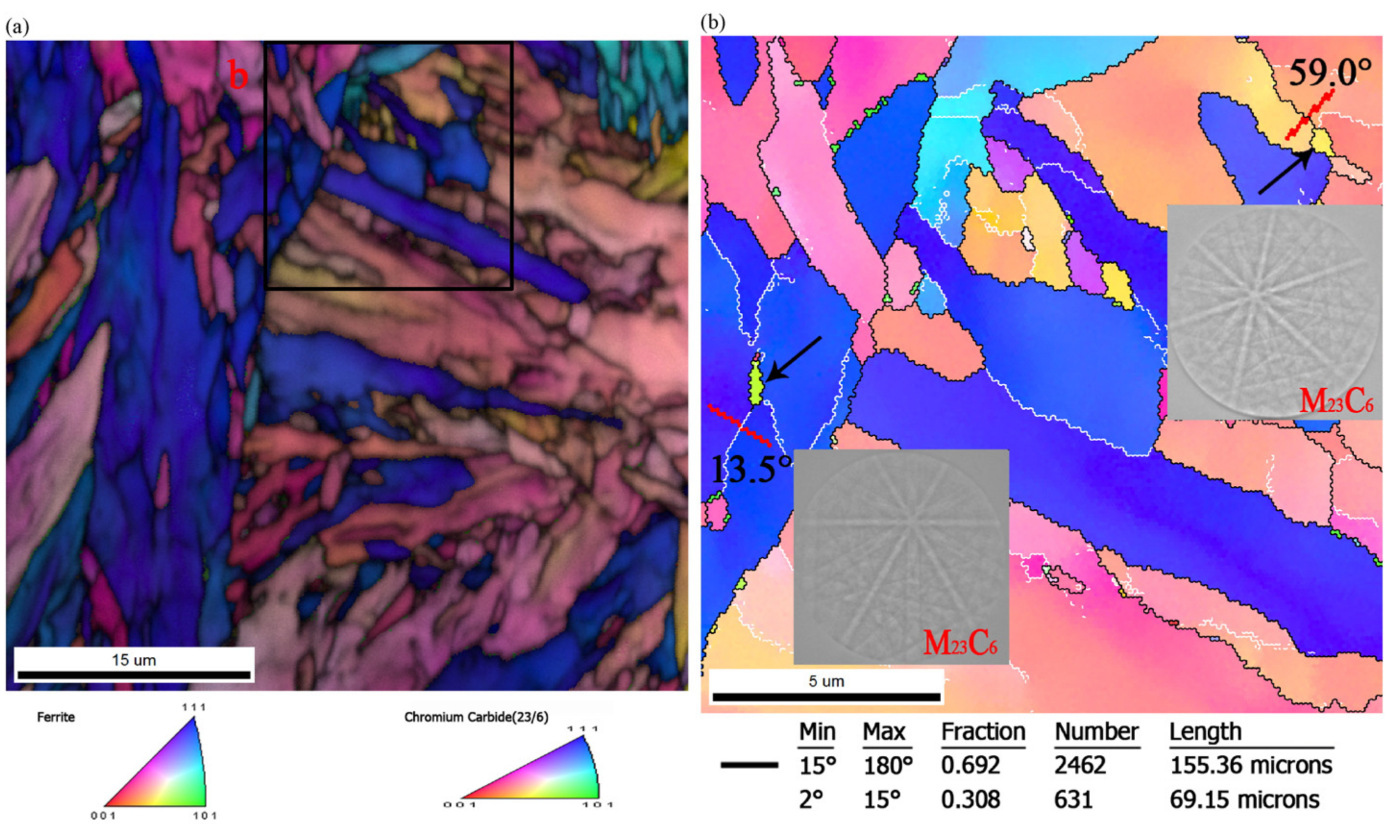

Fig. 1. EBSD map of the 10% Cr steel aged at 650 °C for 4000 h: (a) IQ + IPF, (b) IPF cropped (area b) from (a).