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The abnormal segregation behavior of solutes under tensile stress and its effect on carbide reactions in 2.25Cr–1.5W heat-resistant steels

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ABSTRACT

The phosphorus segregation concentration at grain boundary/carbide interfaces of 2.25Cr–1.5W heat-resistant steels under tensile stress shows a broad convex profile in a log time versus segregation concentration plot. The decrease in phosphorus segregation concentration after the maximum in the convex profile is due to the formation of new equilibrium MC carbides on the surface of the pre-formed $M_{23}C_6$ carbides and its partitioning effect of the phosphorus segregated at the $M_{23}C_6$ carbide interface to the interface of the new MC carbides.

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1. Introduction

In order to release the elastic strain energy caused by the atomic size difference between the solvent and solute and to additionally decrease the interface energy, the solutes segregate toward the interfaces such as free surface and grain boundaries [1,2]. If the system does not show any precipitation reaction directly related to the segregating solute, the grain boundary segregation concentration of the solute increases gradually with increasing time to the equilibrium concentration at the holding temperature [3]. However, if a precipitation reaction related to the segregating solute occurs in the system, the non-equilibrium grain boundary segregation kinetics is significantly affected by the precipitation reaction [4–6]. CrMoV heat-resistant steels with phosphorus content of several hundred ppm show a decrease in grain boundary segregation concentration of phosphorus after a maximum concentration during long-term aging in the temperature range of 480–530 °C [7–9]. Such a segregation phenomenon has been understood in light of the intermetallic quasi-crystalline approximant alloying with phosphorus at the grain boundaries and on the surface of $M_{23}C_6$ carbides [7,8] or in the formation of the M_6C carbides containing molybdenum, iron and phosphorus at the grain boundaries [9]. Recently, it has been reported in 2.25Cr heat-resistant steels with the phosphorus content of several hundred ppm that the phosphorus segregation

to the interface of carbides formed at the grain boundaries and within the matrix is largely influenced by the various carbide reactions occurring in the steels [10–12]. The purpose of this study is to investigate the correlation between non-equilibrium segregation of solutes to the carbide interface and carbide reactions in 2.25Cr–1.5W heat-resistant steels with relatively low bulk phosphorus content.

2. Experimental procedure

Two 2.25Cr–1.5W heat-resistant steels in which the bulk phosphorus content is mainly different were prepared using vacuum induction melting. The chemical compositions of the steels were analyzed by Optical Emission Spectrometer (OES, OBLF QSN-750) and are shown in Table 1. The ingots were homogenized at 1200 °C for 3.6 ks and hot-rolled to 12 mm thick plates. In order to perform stress rupture tests, un-notched cylindrical specimens with a gauge length of 15 mm and a gauge diameter of 6 mm were machined from the plates in the hot-rolling direction. Specimens were austenitized at 1050 °C for 3.6 ks under a vacuum of about 1 Pa and water-quenched in order to obtain a full martensitic structure and to investigate changes in carbide reaction with rupture time. The rupture tests were carried out at 700 °C in the tensile stress range of 75–300 MPa, using conventional creep testers (ATS Lever Arm Type). An N-type thermocouple was attached to the specimens. During heating to the target temperature, the temperature was first raised to 600 °C at a heating rate of 1200 °C/h. But, for precise temperature control, it took about 1.8 ks

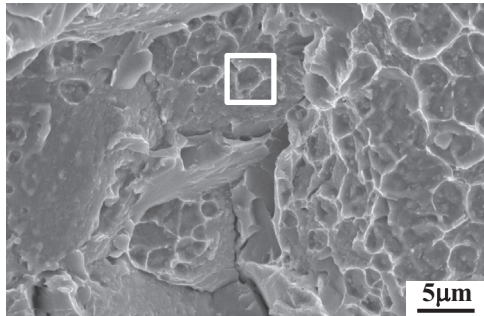
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Table 1

The chemical composition of the prepared steels (wt%).

	C	Si	Mn	P	S	Cr	V	Nb	Ti	W	N	Fe
P130	0.11	0.33	0.50	0.013	0.002	2.26	0.24	0.041	0.002	1.54	0.009	Balance
P310	0.13	0.35	0.50	0.031	0.002	2.27	0.24	0.045	0.002	1.50	0.009	Balance

**Fig. 1.** The fracture surface showing grain boundary/carbide interfaces (GCIs) in the AES specimen of the P310 steel broken under 200 MPa at 700 °C.

from 600 °C to the target temperature 700 °C. The rupture test was performed without soaking at the test temperature. Carbon extraction replica methods were used for the precise analysis of the carbides, using a field-emission transmission electron microscope (FE-TEM, JEOL JEM-2100F) and an energy-dispersive spectroscope (EDS, OXFORD) attached to the FE-TEM. The interfacial segregation behavior of solutes was investigated, using an Auger electron spectroscope (AES, PHI 700). The AES specimens were machined from the ruptured specimens in the tensile stress direction. They were chilled with liquid nitrogen in the AES for 3.6 ks and in situ fractured in vacuum of 9×10^{-8} Pa or better. Typical parameters were the primary electron beam energy of 5 keV and an electron beam size of about 200 nm. About ten points of grain boundary/carbide interfaces (GCIs) were chosen for the AES analysis from the intergranular fracture surfaces of the AES specimen. The GCI means the crater on the grain boundary fracture surfaces where the carbides had resided [10–12] and it is shown in Fig. 1. The AES peaks of Fe₇₀₃, P₁₂₀ and C₂₇₁ were used, and the peak-to-peak height ratio (PHR, I_{Fe}) obtained from the differential AES spectra was averaged.

3. Results and discussion

The non-equilibrium segregation kinetics of phosphorus and carbon at the GCIs are shown in Fig. 2. Fig. 2(c) and (d), which are obtained in the previous researches [11,12], are compared with the present results of Fig. 2(a) and (b). Not only the 1.5% W-added P130 and P310 steels of Fig. 2(a) and (b) but also the W-free P610 steel of Fig. 2(c) shows a broad convex profile in phosphorus segregation concentration in a log time versus segregation concentration plot. In contrast, the W-free P1410 steel of Fig. 2(c) and the 1.5% W-added P600 steel of Fig. 2(d) show two maxima in phosphorus segregation and one minimum between the two maxima. As shown in Fig. 2(c) and (d), the minimum in phosphorus segregation concentration corresponds to the maximum in carbon segregation concentration, which is called the repulsive segregation between carbon and phosphorus [13]. In Fig. 2(a) and (b), the carbon segregation concentration increases slightly in the later time range, while the phosphorus segregation concentration decreases noticeably in both W-added P130 and P310 steels. In order to understand such a segregation behavior of carbon and phosphorus occurring in the 1.5% W-added P130 and P310 steels, carbide reactions were

investigated at the stages *m* and *n* of Fig. 2(a) and (b). Based on the Thermo-Calc [11,12], the equilibrium carbides at 700 °C of the W-free P610 and P1410 steels are M₇C₃ and MC, while the equilibrium carbides of the 1.5% W-added P130, P310 and P600 steels are M₂₃C₆, M₆C and MC. The M₂₃C₆ carbides have the largest phase fraction and the MC carbides have the lowest portion. As shown in Fig. 3(a) and (b), only the equilibrium M₂₃C₆ carbides containing Cr, Fe and V were observed at the stages m1 and n1. At the stage m2 of Fig. 2(a) in which the phosphorus segregation concentration proceeds to decrease, the W-rich M₆C and the V-rich MC carbides were formed on the surface of the M₂₃C₆ carbides of the P130 steel, based on the EDS and the electron diffraction pattern results of Fig. 3(c). Meanwhile, the W-rich M₆C, the V-rich MC carbides and the Nb-rich MC carbides are observed in P310 steel as shown in Fig. 3(d) corresponding to stage n2 of Fig. 2(b). The M₆C carbide seemed to precipitate on the pre-existing M₂₃C₆ carbide. But, as shown in Fig. 4, the M₆C carbide grew rapidly at the stages m3 and n3 of Fig. 2(a) and (b), and then this carbide became much bigger than the preformed M₂₃C₆. Based on the curvature of the interface between the M₂₃C₆ and M₆C carbides of Fig. 4(a), it is reasonable that the coarse M₆C carbide grew mainly at the expense of the M₂₃C₆ carbide. It is shown in Fig. 4(b) that the M₆C carbide on the surface of the M₂₃C₆ carbide also grew into the M₂₃C₆ carbide. In Fig. 3, the strong W concentration around the M₂₃C₆ carbides at the stages m2 and n2 of Fig. 2(a) and (b) is probably not due to the existence of W within the M₂₃C₆ carbides but due to the distribution of the M₆C carbides with various sizes on the surface of the M₂₃C₆ carbides, while the M₆C carbides are not formed at the stages m1 and n1. The formation of the M₆C carbides on the surface of the pre-existing M₂₃C₆ carbides and their growth into the carbide interiors are energetically preferable in satisfying the equilibrium phase fraction of the M₆C carbides, because such a reaction minimizes the total interface energy during its growth and after the growth.

Generally, the carbide transition happens through either the independent nucleation or an in situ transition from the pre-existing carbides [17–22]. The independent nucleation of the carbides was mainly observed in the present study, but the independent carbide nucleation within the matrix can concurrently occur together. Also, the present AES and TEM results and the previous results [11,12] supply an intrinsic clue for the correlation between the solutes' segregation to the carbide interface and various carbide reactions. Before considering the correlation in the present 1.5% W-added P130 and P310 steels with the relatively low bulk phosphorus content, the carbide reactions in the W-free [11] or 1.5% W-added steels [12] showing the two maxima in phosphorus and a minimum in a time versus segregation concentration plot should be understood.

Fig. 5 shows schematic diagrams explaining changes in carbide reactions with tungsten addition and bulk phosphorus content under tensile stress in 2.25Cr heat-resistant steels. As mentioned above, the equilibrium carbides of the W-free steels are M₇C₃ and MC, and those of the W-added steels M₂₃C₆, M₆C and MC. Due to the supersaturated carbon in the martensitic W-free P1410 and P610 steels [11], the non-equilibrium M₃C carbides mainly containing iron are first formed at the grain boundaries or within the matrix at the expense of the supersaturated carbon during heating or rupture test, before the equilibrium carbides are formed. The higher phosphorus segregation concentration (Fig. 2(c)) at the

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