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Microstructure evolution in HR3C austenitic steel during long-term creep at 650 °C

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ABSTRACT

The creep behavior of HR3C austenitic steels was investigated at 650 °C and over the stress range from 150 to 250 MPa for up to 13,730 h. The corresponding microstructure evolution was characterized by optical microscopy (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). In the initial stage of the creep process, the creep-resistance of HR3C steel is enhanced by the precipitation of second-phases particles in the grain and at the grain boundary. Compared with the precipitates inside the grain, the higher nucleation and growth rate of precipitates at the grain boundary is related to the higher interfacial energy and diffusion rate of atoms. The high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) results show that the precipitates inside the grain may initially nucleate at dislocation pile-up sites, and the interface coherency between the precipitate and the matrix can be destroyed after a long-term creep process. The TEM morphology indicates that the agglomerated tiny particles interact with the dislocations, contributing mostly to the precipitation strengthening inside the grain during the long-term creep process at 650 °C, while the growth of chain-like $M_{23}C_6$ precipitates at the grain boundary increases the tendency of intergranular cracking as the creep time increased.

1. Introduction

The demands for clean energy and protection of the global environment have been accelerating for the application of ultra-super critical (USC) power plants. To ensure the safety application under USC conditions, materials with excellent creep strength and corrosion resistance are required. HR3C (25Cr-20Ni-Nb-N) austenitic heat resistant steels are widely used in superheaters and reheaters of steam boilers, which have the most aggressive service environment in USC units [1–3]. HR3C steel is modified from TP310 by the addition of strong carbide/nitride forming elements such as Nb and N to increase the creep strength. The addition of nitrogen in the interstitial sites of the matrix enhances the solid-solution strengthening in the materials, while the dispersively distributed fine NbCrN, $M_{23}C_6$ carbides and Nb-rich carbonitrides in the matrix regions provides precipitation strengthening [4]. The creep rupture strength of HR3C is about 45% higher than that of TP347 at 923 K [5] and HR3C also exhibits higher tensile strength than that of TP347HFG (18Cr-12Ni-Nb) and Super304H (18Cr-9Ni-3Cu-Nb-N) [6]. The resistance to hot corrosion and steam oxidation of HR3C is also superior to conventional 18%Cr heat-resistant steels [4–8].

During the long term service in the temperature regime of 600–700 °C, the microstructure evolution, especially in precipitates, can lead to a degradation of the materials. One of the most successful methods of improving the long-term creep resistance of austenitic steels is to increase the extent of precipitation strengthening during creep exposure. This can be achieved by alloying these steels with small amounts of strongly carbides/nitrides forming elements, such as niobium or nitrogen, or using heat treatment methods. Vodárek [9] found that a small additions of niobium results in a significant reduction of the minimum creep rate and shortening of the tertiary creep stage. Cai et al. [10] discovered an increased amount of nitrogen in solid solution can strengthen the matrix and suppress the coarsening of $M_{23}C_6$ precipitates. Vu The Ha and Woo Sang Jung [11] showed that using the modified thermo-mechanical treatment (MTMT) can doubly increase the creep rupture time, which is due to the improved distribution uniformity of fine nano-sized carbonitride precipitates in the austenitic matrix. As for the effect of temperature on the microstructure evolution during long-term service of this kind of steels, some improvements have been achieved using aging process in numerous works. For example, Peng et al. [12] have reported the influence of the structural evolution on the impact toughness after high temperature

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aging. Wang et al. [13] have studied the evolution process of the precipitated phase during the aging of steel and Bai et al. [14] have investigated the effect of high temperature aging on microstructure and mechanical properties of the steel. As for the creep behavior, more attention is paid to the microstructure characteristics [15], especially the evolution of precipitates during long-term creep test at elevated temperature. During the creep process, the grain boundary (GB) strength can be impaired by the precipitation of intergranular carbides (mostly Fe (Cr, Mo)-rich $M_{23}C_6$). Hong et al. [16] and Jones et al. [17] investigated the relationship between GB characteristics and the formation of intergranular $M_{23}C_6$ precipitates in austensitc steels and found that the presence of $M_{23}C_6$ depends on the GB type: highly random misoriented GBs exhibit more precipitation than ∑3 boundaries. However, not much research has been addressed on the nucleation and growth of phases inside the grain, especially the condition of Z-phase (secondary NbCrN). According to several previous studies, Knowles [18] reported that Z-phase formed from MX precipitates, while Robinson and Jack [19] suggested Z-phase formation from solid solution.

The paper is structured as follows. First, the creep behavior in HR3C steel at 650 °C up to 13,730 h is investigated. The creep results and the micro hardness properties of samples creep-ruptured at different times are next presented. Afterwards, the resulting intergranular damage is assessed using optical and scanning electron microscopy (OM and SEM). In this part, the intergranular cracking and damage are discussed in relation with the mechanical properties above. Finally, the nucleation and growth of precipitates at the grain boundaries and inside the grains are studied using high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED), in which more attention is paid to the interaction between the precipitates and dislocations.

2. Experimental procedures

2.1. Materials

The material chosen for this study is HR3C (25Cr-20Ni-Nb-N) steel, an austenitic heat resistant steel. Its chemical composition specified by standard ASTM is given in Table 1. After the solution treatment at 1230 °C for 30 min, the microstructure of the steel is shown in Fig. 1, in which there is an irregular shaped prime phase inside the grain with a size of 100–200 nm. Energy dispersive X-ray spectroscopy (EDS) analysis shows that the contents of niobium and chromium are relatively high in the prime phase. According to results from previous research [6,20,21], the prime larger phase should be the undissolved Z-phase, which is the prefer sites for the micro crack nucleation during loading process and will have a detrimental effect on the mechanical properties of steel. And the fine precipitates found at the grain boundaries maybe $M_{23}C_6$ carbides, which grow during long term creep process. The twin substructures in the austenite grains are also clear. The mechanical parameters of HR3C steel at room temperature (RT) and 650 °C are shown in Table 2.

2.2. Creep tests

In accordance with ASTM standard E139-06, the creep tests were carried out at 650 °C under constant load conditions and at stress levels of 150, 170, 200, 250 MPa. The temperatures of sample surface were monitored by thermocouple and controlled by an induction heating system. All tests were started after soaking for 30 min at the test temperatures in order to ensure the uniform temperature throughout the samples. Each test ends when the sample fractures at last. The size of creep samples was displayed in Fig. 2.

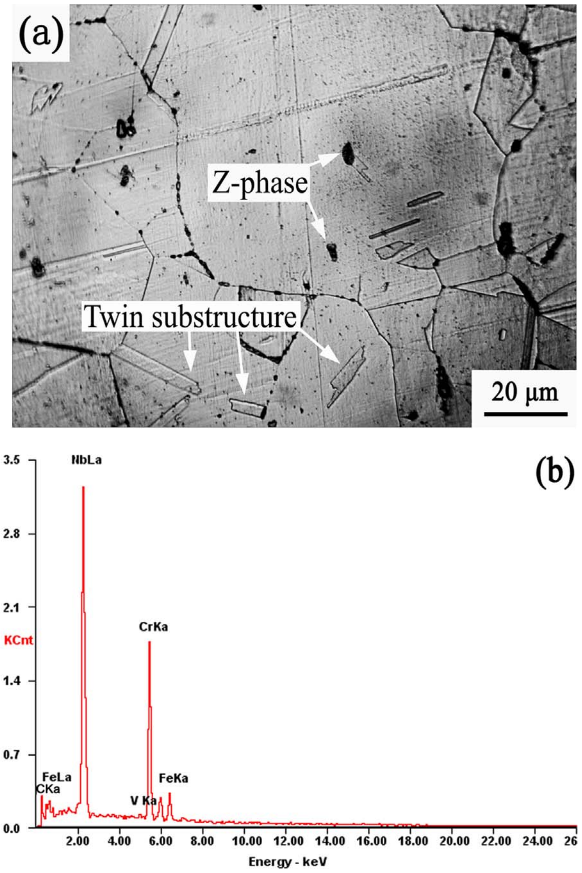

Fig. 1. Optical microscopy image (a) and EDS pattern (b) of as-received HR3C steel.

Table 2
Basic mechanical properties of HR3C steel.

Temperature/°C	0.2% Proof strength/MPa	Tensile strength/ MPa	Elongation/%	Hardness/ HRB
ASME SA-213	≥295	≥655	≥30	≤100
RT	368	740	48	88
650	180	492	45	/

2.3. Microhardness tests

As one of the most important mechanical index of metal materials, the microhardness property can reflect the evolution of microstructure in the materials. In order to exclude a possible influence of the stress level, the change in micro hardness was measured as a function of creep rupture time at constant load condition. The samples for microhardness test are cut from the gauge part of the creep-rupture

Table 1
Chemical composition of HR3C steel (mass percent,%).

	C	Si	Mn	P	S	Cr	Ni	Nb	N
ASTM SA-213	0.04–0.10	≤0.75	≤2.00	≤0.030	≤0.030	24.00–26.00	17.00–23.00	0.20–0.60	0.150–0.350
As-Tested	0.06	0.35	1.18	0.020	0.002	24.84	20.54	0.41	0.230