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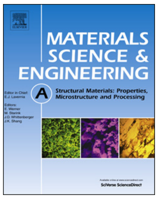

Influence of carbides on the high-temperature tempered martensite embrittlement of martensitic heat-resistant steels

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ABSTRACT

The high-temperature temper embrittlement of martensitic heat-resistant 10Cr12Ni steel was studied. The results demonstrate that there is some irreversible temper embrittlement when the steel is tempered at 625 °C. The irreversible temper embrittlement can be overcome by re-tempering at higher temperature. The tempered martensite embrittlement at 625 °C is attributed to the precipitation of $M_{23}C_6$-type carbides along the martensite lath and prior austenite grain boundaries. The tempering process can be divided into three stages: In the first stage, the martensite laths recover and M_7C_3-type carbides precipitate inside the martensite laths, leading to the improvement of the toughness. In the second stage, M_7C_3-type carbides dissolve, and $M_{23}C_6$-type carbides precipitate along the martensite laths and prior austenite grain boundaries. The $M_{23}C_6$-type carbides play a nucleating role in the development of cracks, leading to tempered martensite embrittlement. In the third stage, the toughness gradually recovers with the further recovery of the martensite laths.

1. Introduction

Martensitic heat-resistant steels containing 9–12% Cr have attracted strong interest for use in the turbine blades of ultra-supercritical power plants because of their high creep strength and high resistance to oxidation and corrosion together with their weldability [1–4]. Brittle failure of turbine blades is one of the most common causes of the failure in ultra-supercritical power plants [5]. Consequently, there is a strong demand for improved fracture toughness in martensitic heat-resistant steels. However, martensitic heat-resistant steels are susceptible to embrittlement by various causes, and temper embrittlement is the most common type of embrittlement. Temper embrittlement has been the subject of many investigations in 9–12% Cr martensitic heat-resistant steels [6–10].

A number of 9–12% Cr martensitic heat-resistant steels have some temper embrittlement at 400–550 °C [9–11]. In the previous studies, the mechanism of the temper embrittlement at 400–550 °C has been sufficiently investigated. The temper embrittlement at 400–550 °C is always reversible and is attributed to the aggregation of phosphorus and chromium at the prior austenitic grain boundaries [8–10]. Additionally, there may also be some high-temperature temper embrittlement above 600 °C in some of the Cr-Ni-Mo-V martensitic heat-resistant steels [10]. However, in the previous century, the steam temperature in power plants has been relatively low and the tempering temperature of the martensitic heat-resistant steels used for turbine blades has always been below 600 °C, so temper embrittlement above 600 °C has not received sufficient attention. In recent years, power plants have been designed with higher steam pressures and higher temperatures to improve their efficiency [12]. This means that a higher tempering temperature must be adopted for these martensitic heat-resistant steels, and temper embrittlement above 600 °C should be taken seriously.

The purpose of this study was to investigate the mechanism of the high-temperature temper embrittlement in martensitic heat-resistant steels. In this paper, the high-temperature temper embrittlement of 10Cr12Ni3Mo2VN steel was studied. This steel is a typical martensitic heat-resistant steel that is used for the last stage turbine blades and always becomes brittle after tempering at either 500 °C or near 620 °C. The temper embrittlement at 500 °C has been proven to be reversible and is caused by the aggregation of impurity elements [6,10,11]. The mechanism of the temper embrittlement at 620 °C has not been studied in depth. In this investigation, the temper embrittlement near 620 °C of 10Cr12Ni steel was found to be connected with the transition of the types of carbides. Consequently, the precipitation behavior of the carbides during tempering and the influence of carbides on the high-temperature temper embrittlement of 10Cr12Ni steel were investigated.

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2. Experimental procedure

The test samples for this study were prepared from a 200-mm diameter 10Cr12Ni annealing bar that was produced by forging from a remelted electroslag ingot. The non-Fe composition, in mass percent, of the experimental steel was: C, 0.12; Si, 0.20; Mn, 0.80; P, 0.020; S, 0.001; Cr, 11.83; Ni, 2.55; V, 0.30; Mo, 1.69; and N, 0.034. To investigate the high-temperature temper embrittlement of the experimental steel, the test samples were oil quenched after austenitizing for 45 min at 1050 °C and later tempered for 0.5–6 h at 575–725 °C. All of the samples after quenching had a similar average prior austenite grain size of approximately 60 μm. The tensile properties were determined using 25 mm gage length cylindrical tensile bars, the impact energy was determined using the standard Charpy V-notch impact test, and the Brinell hardness was also tested.

Optical microscopy (OM), field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) were used to investigate the microstructure of the samples. A scanning electron microscopy (SEM) was used to observe the fracture surface of the impacted specimens. For the OM investigation, the specimens (after heat treatment) were first ground and polished and subsequently etched in a solution of 5 g $CuSO_4$, 70 mL HCl, and 100 mL H_2O. Thin film specimens for the TEM examination were made from slices cut from the specimens after heat treatment that were mechanically ground to a thickness of less than 0.05 mm and electropolished in a solution of 4% perchloric acid in alcohol at −30 °C. A JEM-2100(HR) transmission electron microscope was used to perform the TEM analyses of the thin foil specimens. X-ray energy dispersive spectroscopy (EDS) was used to analyze the composition of the precipitates on the carbon extraction duplicate specimens. To prepare the carbon extraction duplicates, specimens were first prepared as for the optical microscopy investigation; next, a carbon film was deposited on the etched surface, and finally, the carbon film was removed using a solution containing 5 g $CuSO_4$, 70 mL HCl, and 100 mL H_2O.

3. Results

3.1. Mechanical properties

The mechanical properties of the samples after heat treatment are presented in Figs. 1 and 2. A significant tempered martensite embrittlement was indicated by a decrease in both ductility and toughness after tempering at 625 °C in the 10Cr12Ni steel as shown in Fig. 1. Both the strength and hardness decreased as the tempering temperature increased from 575 °C to 725 °C (Fig. 1(a)). The ductility and toughness had minimum values at 625 °C (Fig. 1 (b) and (c)). The impact energy had a different type of variation with the tempering time under different tempering temperatures (Fig. 2). At 575 °C the impact energy rapidly increased with the tempering time below 2 h and changed slowly between 2 and 6 h. At 625 °C the impact energy decreased with the tempering time between 0.5 and 1.5 h and then increased with the tempering time between 1.5–6 h, and reached a minimum value after tempering for 1.5 h. At 675 °C the impact energy consistently increased with increasing tempering time between 0.5 and 6 h. On the other hand, the hardness always decreased as the tempering time increased at every tempering temperature. The temper embrittlement at 625 °C can be eliminated by re-tempering at a higher temperature. If the samples are pre-tempered at higher temperature, the temper embrittlement will not appear after tempering at 625 °C, as shown in Fig. 3. This indicates that temper embrittlement at 625 °C is irreversible in 10Cr12Ni steel.

3.2. Specimen microstructures

The mechanical properties of steel are determined by its microstructure. To investigate the mechanism of the temper embrittlement at 625 °C, the microstructures of the experimental steel after heat treatment were examined. The metallographic images show that the matrix of all of the samples consists of typical temper martensite laths. However, the morphologies of the precipitates are very different after tempering at different temperatures, as shown in Fig. 4. After tempering for 2 h at 575 °C, there are numerous acicular precipitates (with lengths of 300–500 nm) within the martensite laths and the boundaries between the prior austenite grains and the martensite laths are relatively distinct, as shown in Fig. 4(a). The microstructure of these acicular precipitates was examined using TEM, as shown in Fig. 4(d). These TEM micrographs show that these acicular precipitates are composed of numerous smaller short-bar precipitates that have a parallel distribution with a length of less than 50 nm. After tempering for 2 h at 625 °C numerous spherical precipitates formed along the martensite lath and prior austenite grain boundaries, while no acicular precipitates were observed, as shown in Fig. 4 (b) and (e). There are more spherical precipitates after tempering for 2 h at 675 °C compared with 625 °C, as shown in Fig. 4(c) and (f). In addition, numerous finer precipitates were observed in both the quenched and tempered samples, as shown in Fig. 5. The quantity and distribution of the V-rich precipitates have only a little variation with the tempering time and temperature. Furthermore, the V-rich precipitates do not accumulate at the boundaries between the prior austenite grains and the martensite laths.

The types of precipitates in the martensitic heat resistant steels mainly included MX-type, M_2X-type, M_3C-type, M_6C-type, M_7C_3-type, $M_{23}C_6$-type, Laves-type and so on [8,10,11,13]. The diffraction pattern and the chemical composition of theses precipitates were analyzed to identify the types of the precipitates in the

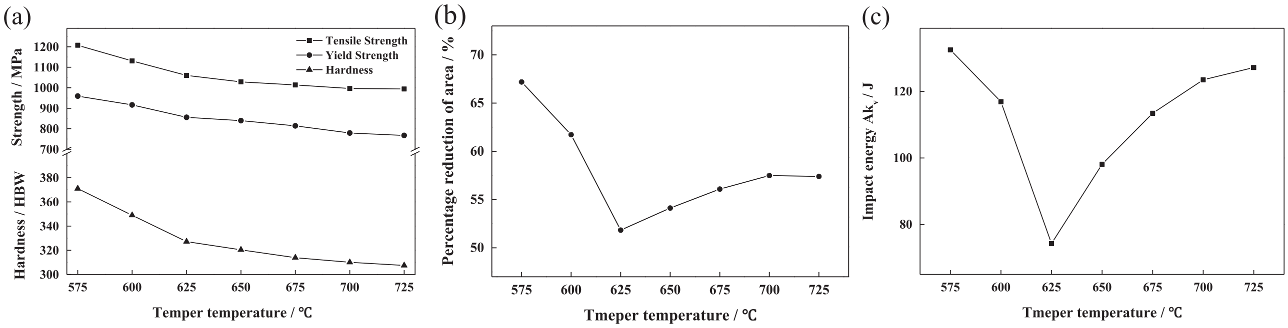

Fig. 1. The mechanical properties of the experimental steel after tempering for 2 h at different temperatures.