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Alloy carbide precipitation in tempered 2.25 Cr–Mo steel under high magnetic field

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Abstract

The influence of a high magnetic field on carbide precipitation during the tempering of a 2.25 Cr–Mo steel was investigated by means of transmission electron microscopy. As-quenched specimens were tempered at 200, 550 and 700 °C for various times in the absence and presence of a 12 T magnetic field. Experimental results indicate that the applied high magnetic field effectively promotes the precipitation of $M_{23}C_6$ carbides at low temperature (200 °C) and M_7C_3 and $M_{23}C_6$ carbides at intermediate temperature (550 °C). The increased Fe content in the $M_{23}C_6$ and M_7C_3 carbide significantly increases the magnetization. The magnetic Gibbs free energy, which influenced the alloy carbide precipitation behavior, was considered to be mainly determined by the intrinsic magnetization energy for $M_{23}C_6$ and M_7C_3 carbides. With the increase of the tempering temperature (700 °C), there was no pronounced effect of the high magnetic field on the precipitation sequence and the concentration of substitutional solute atoms in paramagnetic carbides. The investigation of alloy carbide precipitation under high magnetic fields could contribute to a better understanding of phase transformation of alloy carbides and to the heat treatment and fabrication of heat-resistant steels.

Keywords: Steels; Carbide; Precipitation; Transmission electron microscopy; High magnetic field

1. Introduction

2.25 Cr–Mo steel has been widely used for pressure vessels and piping because of its excellent elevated-temperature strength and resistance to hydrogen attack. Alloy carbides play an important role in heat-resistant steels, including those which are microalloyed or secondary-hardened for service at elevated temperatures. M_3C, M_2C, M_7C_3, $M_{23}C_6$, etc., are the most important precipitate phases in 2.25 Cr–Mo powerplant steels. Many of them are metastable at lower temperatures but it is important to understand their behavior and effects since they can nucleate easily and some of them may become stable during service.

M_7C_3 and $M_{23}C_6$ (M = Fe, Cr, Mo or Mn, etc.) are the predominant precipitates in Cr–Mo steels [1]. Generally, the multi-component alloy carbide contains more than one metallic element. The quantitative calculations of the stability of carbides [2,3] indicate that the replacement of some of the chromium atoms by iron influences the stability of carbides. First-principles calculation has revealed that the pure $M_{23}C_6$ (M = Fe) is more stable than commonly occurring θ-Fe_3C and more $M_{23}C_6$ are expected in steels [4]. The substitution of chromium for iron favors the thermal stability of the Fe_7C_3-type structure phase and influences the magnetic properties [5].

The application of a high magnetic field during phase transformations of metallic materials has attracted significant attention since the late 1980s because it is a new approach for modification of microstructure and thus property optimization [6–16]. If the parent and product phases have different saturation magnetization and are

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open to transformation under the magnetic field, the temperature and extent of transformation can be considerably affected as the Gibbs free energy of a phase can be lowered by an amount corresponding to its magnetization [7,17] This effect was first investigated theoretically and experimentally using several ferroalloys undergoing non-diffusion martensitic transformation [18,19]. So far, the research on this topic focuses on the following aspects: martensitic [20–22], bainite [23], ferrite [15] and pearlite [24] transformations, the nucleation and growth of cementite [25] and carbide precipitation [16]. Although some progress has been made, the effects of magnetic field on alloy carbide formation need further research. The present work was undertaken to study mainly the precipitation behavior of alloy carbide in 2.25 Cr–Mo steel under a 12 T magnetic field. Insights into these aspects are expected to contribute to a better understanding of alloy carbide in reduced activation steels used in magnetic confinement Tokamak, which is long-term exposition under high temperature and high magnetic field in a nuclear fusion reactor [26].

2. Experimental and calculation

2.1. Experimental procedures

2.25 Cr–Mo commercial steel, of chemical composition (wt.%) 0.1 C, 0.30 Si, 0.50 Mn, 1.00 Mo, 2.20 Cr and balance Fe, was prepared by vacuum refining, continuous casting, hot-rolling and finally normalizing. Specimens were made to a square column of $7 \times 7 \times 25\ mm^3$, which was suitable for the magnetic field heat treatment furnace followed by ice brine quenching to obtain a martensite microstructure for subsequent tempering. The specimens were heat-treated at 200, 550 and 700 °C for 600 s and 3600 s with and without a 12 T magnetic field.

Carbon or gold replica specimens were examined in a JEM-2010 HT microscope operating at 200 kV for selected-area electron diffraction (SAED) analysis to observe the microstructure. A JEM-2100F microscope equipped with an energy-dispersive spectroscopy (EDS) system was mainly used to analyze the compositions of carbides. Specimens with 3 mm diameter were hot mounted with bakelite molding powder, and ground with silicon carbide paper down to 2000 grit and then polished with Al_2O_3 with a particle size of 0.5 μm. They were then deeply etched with a 4 vol.% nital for a few seconds. A carbon or gold coating of 20–30 nm was deposited in a vacuum system. This film was then scored with a sharp blade to divide it into several smaller squares ($\sim 1\ mm^2$). Then, chemical etching in nital solution (8 vol.%) was conducted to remove the carbon or gold film with the extracted carbides. The carbon or gold film was washed in methanol and floated off in distilled water to flatten the film. Finally, these small films were mounted on copper grids for TEM analysis. 45 isolated particles of $M_{23}C_6$ and 35 isolated carbides of M_7C_3 were analyzed for the specimens tempered at 200 °C for 6 h with and without a magnetic field, respectively. More than 50 and 25 isolated particles of $M_{23}C_6$ and M_7C_3, respectively, from the specimens tempered at 550 °C for 3600 s with the magnetic field were examined. 70 isolated particles of $M_{23}C_6$ carbides were selected for EDS examination for the specimens tempered at 700 °C for 6 h with and without a 12 T magnetic field. A photograph was taken for each individual particle analyzed in order to correlate the particle size with composition. Care was taken to ensure that unbiased distributions of particle sizes were studied.

2.2. First-principles calculation of different carbides

The all-electron full-potential linearized augmented-plane wave (FP-LAPW) method was used as embodied in the WIEN2K code [27]. The exchange–correlation potential was calculated using the generalized gradient approximation (GGA) via the scheme of Perdew–Burke–Ernzerhof 96 (PBE-GGA) [28]. The electronic wave functions were sampled with 47 k and 72 k points in the irreducible Brillouin zone of $Cr_xFe_{23-x}C_6$ and $Cr_xFe_{7-x}C_3$, respectively. The use of the full potential ensured that the calculation was completely independent of the choice of the sphere radii. Different plane waves were tested, e.g. 2390–2415 grids for $Cr_xFe_{23-x}C_6$ and 1630–1645 grids for $Cr_xFe_{7-x}C_3$.

3. Results

3.1. Precipitation sequence of alloy carbide at 200 °C

Fig. 1 shows the TEM micrographs and the corresponding SAED patterns of the carbides in the specimens tempered at 200 °C for 3600 s without and with the presence of magnetic field of 12 T. It can be observed that in the case of no magnetic field the two kinds of M_2C and M_3C carbides were precipitated. However, after a 12 T magnetic field was applied the alloy carbide $M_{23}C_6$ was identified by means of the SAED pattern. The precipitation sequence is shown in Table 1. Four kinds of alloy carbides, M_2C, M_3C, M_7C_3 and $M_{23}C_6$, were precipitated in the tempered specimens. When the 12 T magnetic field was not applied, only M_2C, M_3C and M_7C_3 carbides were precipitated over 3600 s. In contrast, when a 12 T magnetic field was applied, $M_{23}C_6$ was precipitated in all the stages. The high magnetic field promoted the precipitation of the alloy carbide $M_{23}C_6$.

The concentration of substitutional solute atoms of Fe, Cr, Mo and Mn in the $M_{23}C_6$ was measured, as listed in Table 2. The measured Fe concentration was apparently much higher than the equilibrium concentrations calculated by Thermo-Calc [29] software. The crystal structure of $M_{23}C_6$ is very complex. The carbides $M_{23}C_6$ precipitated from multi-component alloys generally contain more than one metallic element. Because the content of Mo and Mn is significantly less than that of Cr, for simplicity, only the Cr and Fe atoms were considered in the $M_{23}C_6$