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Refining effect of TiC on primary M_7C_3 in hypereutectic Fe–Cr–C harden-surface welding coating: Experimental research and first-principles calculation

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ABSTRACT

Hypereutectic Fe–Cr–C coatings with and without Ti additive were developed by harden-surface welding. The equilibrium phase diagrams of the coatings were calculated by Thermal-calc software. The phase structures were determined by X-ray diffractometer (XRD). The microstructures were observed by optical microscopy (OM). The micro-morphologies of M_7C_3 and TiC were observed by field emission scanning electron microscopy (FESEM). The compositions of M_7C_3 and TiC were determined by energy dispersive spectrum (EDS). The crystal structure of primary M_7C_3 was determined by transmission electron microscopy (TEM). The phase diagrams indicate that TiC precipitates firstly in the coating with Ti additive. The subsequent phase transformation is the same as that in the coating without Ti additive, namely primary M_7C_3 precipitates and then eutectic reaction occurs. The XRD patterns are corresponding to the phase diagrams, which show that there exists TiC in the coating with Ti additive. By comparing their metallographic images, the primary M_7C_3 are obviously refined in the coating with Ti additive. From the micro-morphologies of M_7C_3 and TiC, it is found that TiC exists inside primary M_7C_3 and they are tightly combined. Therefore, TiC may be the heterogeneous nucleus of primary M_7C_3. On the basis of experimental research, the refining effect of TiC on primary M_7C_3 was investigated by first-principles calculation. The calculation results shows the work of adhesion of $Fe_3Cr_4C_3(0001)/TiC(111)$ interface is 3.48 J/m^2 and the interfacial energy ranges from 0.921 J/m^2 to 2.782 J/m^2. The $Fe_3Cr_4C_3(0001)/TiC(111)$ interface is theoretically stable. The $Fe_3Cr_4C_3(0001)/TiC(111)$ interface is well jointed by Ti–C polar covalent/ionic bond and Cr–Ti metallic bond. Therefore, the preferentially precipitated TiC in Fe–Cr–C–Ti alloy is the heterogeneous nucleus of primary M_7C_3 and thereby refines the primary M_7C_3.

1. Introduction

Hypereutectic Fe–Cr–C harden-surface welding coating is the most common material for surface hardening, whose abrasive resistance is mainly attributed to the primary M_7C_3 [1–3]. While, the coarse primary M_7C_3 often causes cracks during the solidification process and makes itself to peel off during application, which may reduce the abrasive resistance of the hypereutectic Fe–Cr–C harden-surface welding coating [2,4,5]. Grain refinement is a kind of effective method to improve the anti-crack property of the harden-surface welding coating during solidification as well as promote its strength and toughness [6,7], which attracts great interest of experts on surface coating. There are numerous ways to refine the primary M_7C_3 in hypereutectic Fe–Cr–C harden-surface welding coating, such as rapid cooling [8,9], lowing overheating [10] and semi-solid processing [11]. However, alloying treatment is the most economical and effective way to refine the primary M_7C_3.

The primary M_7C_3 in hypereutectic Fe–Cr–C harden-surface welding coating can be refined by adding different alloy additives into the welding materials. X.W. Qi et al. [12] investigated the microstructure and mechanical properties of Fe–Cr–C harden-surface welding coating with V additive, which indicates that V can refine the primary M_7C_3, and abrasive resistance of the coating

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is improved accordingly. J. Yang et al. [13] compared the effect of La additive on the primary M_7C_3 in hypereutectic Fe–Cr–C harden-surface welding coating, which reveals that the size of the primary M_7C_3 is decreased with increasing La additive. X.H. Zhi et al. [14] found that the primary M_7C_3 in hypereutectic Fe–Cr–C harden-surface welding coating can be refined by adding Ce additive and the impact toughness of the coating is promoted dramatically. It has also been proved to be valid for refining primary M_7C_3 by adding Y additive in hypereutectic Fe–Cr–C harden-surface welding coating [15].

Ti is the most common alloying element that can refine the primary M_7C_3 significantly. X.H. Zhi et al. [16] proved that TiC is preferentially formed during the solidification process of the hypereutectic Fe–Cr–C harden-surface welding coating with Ti additive. The lattice mismatch between TiC(110) and M_7C_3(010) is 10.0%, so TiC can be heterogeneous nucleus of primary M_7C_3 and thereby refines it. Y.F. Zhou et al. [17] found that with higher Ti additive, the mass loss of the Fe–Cr–C alloy during abrasion is decreased, which means that the wear-resistance is improved. Although the heterogeneous nucleation mechanism can be explained by lattice mismatch theory, the refining effect is also related to the interface stability and electronic structure of M_7C_3/TiC interface. While the micro interfacial behaviors of M_7C_3/TiC interface has never been reported so far.

Nowadays, first-principles method has been widely used in graphene materials, boron nitride superhard materials, magnesium and aluminum materials as well as steel materials [18–20]. The bulk properties such as structural stabilities, electric properties and magnetic properties can be predicted by first principles method, which is lower-cost and higher-efficient than experimental method. Besides predicting the bulk properties, first-principles method can also be applied in investigating the interfacial behaviors such as the interfacial combination, interfacial electronic structure and bonding [21,22].

In this paper, the refining effect of TiC on the primary M_7C_3 is observed and analyzed by experimental method. Then the interface stability and electronic structure of M_7C_3/TiC interface are calculated by first-principles method. So that the refining effect of TiC on primary M_7C_3 in hypereutectic Fe–Cr–C harden-surface welding coating is revealed from experimental phenomenon and micro interface behavior.

2. Experimental and calculation methods

2.1. Experimental method

The experimental materials were two kinds of hypereutectic Fe–Cr–C harden-surface welding coatings with and without Ti additive, whose chemical compositions are listed in Table 1. The element contents of the coatings are similar except for Ti. Because Ti is strong carbide forming element and the eutectic compositions of the coating may be changed if a large number of TiC is formed [23], the Ti content in this paper is only 0.60%. The coating without Ti additive is named as Fe–Cr–C alloy, whereas the coating with 0.60% Ti content is named as Fe–Cr–C–Ti alloy in this paper. According to Table 1, the equilibrium phase diagrams were calculated by Thermal-Calc 4.0 software.

Table 1
Chemical composition of Fe–Cr–C alloy and Fe–Cr–C–Ti alloy (wt%).

	C	Cr	Si	Mn	V	Ti	Mo	Fe
Fe–Cr–C alloy	3.69	26.30	0.93	1.42	0.11	0	0.16	Bal.
Fe–Cr–C–Ti alloy	3.71	26.31	0.96	1.39	0.10	0.60	0.15	Bal.

Specimens with 10 mm × 10 mm × 10 mm were cut from Fe–Cr–C alloy and Fe–Cr–C–Ti alloy. The surfaces of the specimens were prepared by grinding and mechanical polishing. Then the specimens were examined by D/max-2500/PC X-ray diffractometer (XRD) with Cu Kα radiation (20–120°, 1°/s). The polished specimens were dyed with 25%$K_3Fe(CN)_6$+7%NaOH+68%H_20 solution and then observed by Axiovert 200 MAT optical microscopy (OM). The polished specimens were also etched with 50%HCl+50% C_2H_5OH solution and then the micro-morphologies of M_7C_3 and TiC were observed by Hitachi S3400 N field emission scanning electron microscopy (FESEM) and their compositions were determined by energy dispersive spectrum (EDS). The foil specimens about 300 μm thick were ground to about 60 μm and then thinned by Gatan precision ion polishing system (PIPS). Then the specimens were observed by JEM-2010 transmission electron microscopy (TEM) and the results were analyzed by DigitalMicrograph 3.10.0 software. Nano-mechanical tester (TriboIndent) with load of 9 mN and dwell time of 10s was conducted for primary M_7C_3 hardness determination.

2.2. Calculation method

The density functional theory (DFT) as implemented in the Cambridge Sequential Total Energy Package (CASTEP) was employed to calculate the interface stability and electronic structure of M_7C_3/TiC interface in this paper. The generalized gradient approximation (GGA) of Perdew and Wang (PW91) was employed for evaluation of the exchange-correlation energy according to the literature [24]. A 350eV plane-wave cutoff energy and k-point samplings of 4 × 4 × 6 and 6 × 6 × 6 were adopted for bulk M_7C_3 and bulk TiC respectively. In the convergence testing calculation, a 350eV plane-wave cutoff energy and k-point samplings of 4 × 4 × 1 and 6 × 6 × 1 were adopted for M_7C_3 slabs and TiC slabs respectively. A 350eV plane-wave cutoff energy and k-point samplings of 4 × 4 × 1 were adopted for interface calculation. Although first-principles calculation obtains data at T = 0 K, it has accounted for many experimental phenomena at T > 0 K till now [25].

3. Experimental results

3.1. Phase diagrams

The phase diagrams of Fe–Cr–C alloy and Fe–Cr–C–Ti alloy are shown in Fig. 1, in which the C content of the alloys are marked by dashed lines. According to Fig. 1a, primary M_7C_3 precipitates firstly during the solidification process of Fe–Cr–C alloy. Then eutectic M_7C_3 and austenite generate simultaneously in eutectic reaction until the molten alloy completely transforms into M_7C_3 and austenite. According to Fig. 1b, TiC precipitates firstly during the solidification process of Fe–Cr–C–Ti alloy and then primary M_7C_3 precipitates. The subsequent phase transformation is the same as that in Fe–Cr–C alloy until the molten alloy completely transforms into TiC, M_7C_3 and austenite. By comparing Fig. 1a and b, the eutectic C contents of Fe–Cr–C alloy and Fe–Cr–C–Ti alloy are both 2.7%.

3.2. XRD patterns

The XRD patterns of Fe–Cr–C alloy and Fe–Cr–C–Ti alloy are shown in Fig. 2. From Fig. 2a, Fe–Cr–C alloy mainly contains M_7C_3 and γ-Fe (austenite). From Fig. 2b, Fe–Cr–C–Ti alloy contains a certain amount of TiC, besides of M_7C_3 and γ-Fe. The XRD patterns are consistent with the phase diagrams in Fig. 1.