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Refinement and homogenization of M_7C_3 carbide in hypereutectic Fe-Cr-C coating by Y_2O_3 and TiC

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ABSTRACT

The microstructures of the hypereutectic Fe-Cr-C, Fe-Cr-C-Ti and Fe-Cr-C-Ti-Y_2O_3 coatings were observed by OM. The phase structures were characterized by XRD and XPS. The elemental distributions were analyzed by EDS. The interface relationship between TiC and nano-Y_2O_3 were observed by TEM and analyzed by lattice misfit theory. From the metallographic observations, the primary M_7C_3 carbide can be refined by Ti additive, while it is inhomogeneously distributed. However, the primary M_7C_3 carbide can also be refined further by adding Ti additive and nano-Y_2O_3 simultaneously, and it is homogeneously distributed. From the phase constituent analysis, TiC is formed by Ti additive, while TiC and Y_2O_3 are found by adding Ti additive and nano-Y_2O_3 simultaneously. From the elemental distribution mappings and TEM images, TiC nucleates upon nano-Y_2O_3 with orientation relationship $\{001\}_{Y2O3}//\{001\}_{TiC}$ in the hypereutectic Fe-Cr-C-Ti-Y_2O_3 coating. By misfit computation, the lattice misfit between Y_2O_3 (001) plane and TiC (001) plane is 7.3%, which suggests that Y_2O_3 can act as the heterogeneous nucleus of TiC so that TiC particles are increased and dispersedly distributed. These numerous dispersed TiC particles can further act as the heterogeneous nucleus of the primary M_7C_3 carbide, which play a role in refining primary M_7C_3 carbide and promoting its homogenization.

1. Introduction

With excellent wear-resistance, hypereutectic Fe-Cr-C coating has aroused wide concern in the arc surfacing additive manufacturing field [1,2]. However, as the main strengthening phase, the primary M_7C_3 carbide is easy to desquamate from the substrate due to its coarse size [3,4], which restricts the application of hypereutectic Fe-Cr-C coating in 3D-printing field.

Currently, ceramic phases such as TiC, which can play a role in refining the microstructure as heterogeneous nucleus, have been widely applied as reinforced particles in coatings to enhance the wear-resistance [5,6]. G. S. P. Kumar et al. [7] studied the microstructure of in situ fabricated AA6061-TiC composite and found that grains are refined due to the dispersed TiC particles. S.M. Hong et al. [8] added nano-sized TiC particles into SA-106B carbon steel and found that the grain size was reduced considerably with an increase in the TiC content.

In recent years, rare earth oxides have attracted great attention of researchers for their modifying, refining and purifying effects [9–11]. Many investigations show that rare earth oxides doped composites possess finer structures. J.F. Li et al. [12] investigated the effect of La_2O_3 additions on grain size of La_2O_3/W composite, and the results demonstrate that its mean grain size is decreased by La_2O_3. H.X. Qu et al. [13] studied the effect of CeO_2 on the microstructure of WC-40%Al_2O_3 composite, which reveals that CeO_2 promotes its microstructural refinement.

Our research group have added Ti/Nb additives into hypereutectic Fe-Cr-C coating by arc surfacing welding method and found that the previously precipitated MC (namely TiC and NbC) particles can act as the heterogeneous nucleus of the primary M_7C_3 carbide and thereby refines it [14,15]. We have also doped rare earth oxides such as La_2O_3, Y_2O_3 and CeO_2 into hypereutectic Fe-Cr-C coating, and found that they can also act as the heterogeneous nucleus and refine the primary M_7C_3 carbide [16–18]. However, if Ti/Nb additives and rare earth oxides are added into hypereutectic Fe-Cr-C coating simultaneously, whether the microstructure of the hypereutectic Fe-Cr-C coating can be further refined or not? At present, no researches have been reported.

In this paper, hypereutectic Fe-Cr-C, Fe-Cr-C-TiC and Fe-Cr-C-TiC-Y_2O_3 coatings were prepared by arc surfacing welding method. Based on the work that Ti additive was added, nano-Y_2O_3 particles were further added in order to investigate the refining effect of TiC and Y_2O_3

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Table 1
Parameters of welding process.

Wire diameter (mm)	Welding voltage (V)	Welding current (A)	Welding speed (mm·min^{-1}.)
3.2	24–26	200–224	300

on the primary M_7C_3 carbide in hypereutectic Fe-Cr-C-TiC-Y_2O_3 coating, which can provide the foundation for the wide application of hypereutectic Fe-Cr-C coating in 3D-printing field.

2. Experimental Methods

Three kinds of flux-cored wires were prepared by the following procedures. The mineral powders were mixed by using a three dimensional vibratory mill of 1400 r/min for 2 h. The H08A steel strip took "U" shape after multiple rolling. Then the fully mechanical-mixed powders were synchronously delivered to the U-shaped groove and the H08A steel strip passed through multiple forming-rollers step-by-step. Finally the O-shaped flux-cored wire was produced. In order to investigate the effect of TiC, ferro-titanium powder (d ≈ 200 μm) was added. In order to investigate the effect of TiC and Y_2O_3, ferro-titanium powder and nano-Y_2O_3 powder (d ≈ 200 nm) were added simultaneously. The flux-cored wires were cladded on SS41 substrate by ZXG3–300-1 DC welder machine, by which hypereutectic Fe-Cr-C coating (wt%: 3.5C + 26.7Cr + 1.0Si + 1.4Mn + 0.1 V + 0.1Ni + 0.5Al + Bal. Fe), hypereutectic Fe-Cr-C-Ti coating (adding 0.5 wt %Ti on the basis of hypereutectic Fe-Cr-C coating) and hypereutectic Fe-Cr-C-Ti-Y_2O_3 coating (adding trace amount of nano-Y_2O_3 on the basis of hypereutectic Fe-Cr-C-Ti coating) were prepared. The welding parameters are listed in Table.1.

Samples were polished and etched with 35%$FeCl_3$ + 6% HNO_3 + 2%HCl + 57%C_2H_5OH solution. And then microstructures were observed by Axiovert 200 MAT optical microscope (OM). The size of the primary M_7C_3 carbides were analyzed by Image-pro Plus 5.1.0 software. On account that the primary M_7C_3 carbide is irregular polygon, area statistics were used for size characterization for convenience. The coatings were detected by D/max-2500/PC X-ray diffractometer (XRD). The surface composition of the hypereutectic Fe-Cr-C-Ti-Y_2O_3 coating was measured by Thermo VG Multilab2000 X-ray photo-emission spectroscopy (XPS). The elemental distributions of the coatings were measured by EMAX energy dispersive spectrometer. In addition, foil specimen cut from hypereutectic Fe-Cr-C-Ti-Y_2O_3 coating was mechanical polished and thinned by Gatan precision ion polishing system (PIPS). Then the foil specimen was observed by JEM-2010 transmission electron microscopy (TEM). The dispersion of TiC in Fe-Cr-C-Ti and Fe-Cr-C-Ti-Y_2O_3 coatings were observed by Hitachi S3400 N back-scattering scanning electron microscope (BSEM).

3. Results and Discussion

3.1. Size and Distribution of Primary M_7C_3 Carbide

Fig. 1 shows the metallographic images of the coatings, in which the white irregular polygons are the primary M_7C_3 carbides. The mean sizes of the primary M_7C_3 carbides in hypereutectic Fe-Cr-C, Fe-Cr-C-Ti and Fe-Cr-C-Ti-Y_2O_3 coatings are 434.7 μm^2, 168.8 μm^2 and 94.2 μm^2 respectively. From Fig. 1a and Fig. 1b, it is demonstrated that the primary M_7C_3 carbide can be refined by Ti additive, which is in consistence with previous researches [14,19]. The refinement is ascribed to the heterogeneous nucleus role of TiC to primary M_7C_3 carbide. From Fig. 1b and Fig. 1c, the size of the primary M_7C_3 carbides becomes even smaller by nano-Y_2O_3, which means that adding Ti additive and nano-Y_2O_3 into hypereutectic Fe-Cr-C coating simultaneously can further refine the primary M_7C_3 carbides. It also can be found from Fig. 1 that adding Ti and nano-Y_2O_3 simultaneously can promote the uniform distribution of the primary M_7C_3 carbides.

Fig. 2 shows the size statistics of the primary M_7C_3 carbides in the coatings, in which each point represents a primary M_7C_3 carbide. It is found that the size span of the primary M_7C_3 carbides in hypereutectic Fe-Cr-C coating is the maximum, where the majority carbides are smaller than 1000 μm^2, while the minority carbides are larger than 1000 μm^2 and even several carbides reach 3000 μm^2. Relatively, the majority carbides in hypereutectic Fe-Cr-C-Ti coating are smaller than 500 μm^2, and only few are in the range of 500 μm^2–1000 μm^2. While, the size span of the primary M_7C_3 carbides in hypereutectic Fe-Cr-C-Ti-Y_2O_3 coating is quite small. The size statistics fluctuate near the mean size and only individual carbides reach 300–400 μm^2. Fig. 2 illustrates that the dimension uniformity of the primary M_7C_3 carbides can be improved by adding Ti and nano-Y_2O_3 simultaneously.

3.2. Phase Constituent Analysis

Fig.3 displays the XRD patterns of the coatings. It can be seen that the hypereutectic Fe-Cr-C coating mainly contains M_7C_3 carbide, γ-Fe (austenite). While the hypereutectic Fe-Cr-C-Ti and Fe-Cr-C-Ti-Y_2O_3 coatings also contain TiC besides of these two phases. However, Y_2O_3 is not detected in hypereutectic Fe-Cr-C-Ti-Y_2O_3 coating, which may be due to the trace amount of nano-Y_2O_3.

Fig. 4a shows the XPS spectra of the hypereutectic Fe-Cr-C-Ti-Y_2O_3 coating, which is calibrated with respect to the peak of C element. Y-3d peaks are found in the range of 150 eV–170 eV. Fig. 4b shows the XPS spectra of the Y-3d region. Two distinct peaks at 156.5 eV and 161.1 eV can be assigned to $3d_{5/2}$ and $3d_{3/2}$ of Y^{3+} respectively, which proves the existence of Y_2O_3 in hypereutectic Fe-Cr-C-Ti-Y_2O_3 coating.

3.3. Heterogeneous Nucleus Analysis

Fig. 5 shows the elemental distribution mappings of the hypereutectic Fe-Cr-C-Ti-Y_2O_3 coating. Based on the fact that the primary

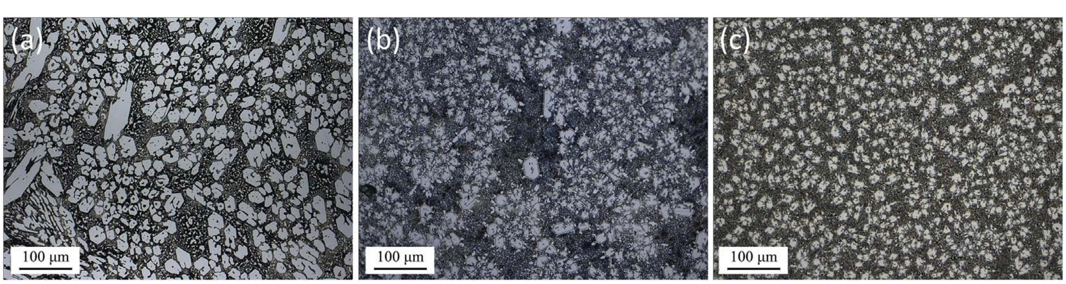

Fig. 1. Microstructures of (a) hypereutectic Fe-Cr-C coating, (b) hypereutectic Fe-Cr-C-Ti coating and (c) hypereutectic Fe-Cr-C-Ti-Y_2O_3 coating.