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Evaluation of microstructure and growth kinetics of tungsten carbide ceramics at the interface of iron and tungsten

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ABSTRACT

The microstructure evolution and growth kinetics of tungsten carbide (WC or W_2C) ceramics at the interface of iron and tungsten during isothermal annealing process from 1100 °C to 1150 °C were investigated by X-ray diffraction (XRD), electron backscattered diffraction (EBSD) and scanning electron microscopy (SEM), respectively. The results show that carbide formation that involves W_2C, WC and a small quantity of Fe_2W_2C, is strongly dependent on a diffusion-controlled reaction. During the evolution process of tungsten carbides, W_2C emerges as an initial phase by the reaction of W and C, and WC is formed as the second phase, because the value of Gibbs free energy of formation of W_2C is more negative than that of WC at the annealing temperature. The initial W_2C transforms into WC until complete consumption of the W_2C. Additionally, Fe_2W_2C between W_2C and WC was formed at a relatively low temperature (1100 °C and 1125 °C) with a long annealing time (60 min). After the W_2C is consumed completely, WC grows by C diffusion, where the growth kinetics of a dominant WC ceramic exhibits a parabolic growth law before metal tungsten is completely consumed. The growth activation energy of the WC layer is calculated to be achieved with a value of 208.68 kJ/mol. When the metal tungsten is completely consumed after annealing at 1150 °C for 60 min, the W_2C and Fe_2W_2C disappear, and only the WC phase exists in the final product.

1. Introduction

Iron-based composites with tungsten carbide ceramics as the reinforcements have been widely investigated due to their high stiffness, high strength, and improved resistance to creep, fatigue and wear [1–4]. These mechanical behaviours make these composites promising structural materials for industry applications [2,3,5]. Grey cast iron is applied extensively in the mining and automobile industries, such as in the manufacturing of disk brakes, where resistance to wear is a crucial requirement [6,7]. Hence, it is important to prepare tungsten carbide ceramics reinforced iron matrix composites (CRIMCs), investigate their microstructure, and improve their mechanical performance to broaden their applications. Previous studies indicate that a wide range of processes were utilized to obtain WC-iron composites, such as spark plasma sintering [1,8], laser melting deposition [3,4], hot pressing sintering [9,10] and in situ synthesis (ISS) [11,12]. During these processes, the ISS technique through isothermal annealing is considered to be one of the most promising methods for the production of tungsten carbide CRIMCs because of the relatively good wettability and strong interfacial bonding between the tungsten carbide ceramic and the iron matrix [4], as well as the cost savings [12].

The effects of the process parameters on the microstructure of tungsten carbide ceramics, coatings, hard metals and composites have been extensively investigated [13–18]. The influence of Ni3Al content on the WC morphology was revealed through the evolution of the microstructure of WC grains in WC-Co-Ni-Al alloys [14]. To optimize the conditions for achieving a sound coating, the effects of the process parameters on the coating features were investigated [15]. Additionally, the densification and grain-growth kinetics of tungsten carbide ceramics in the sintering process were reported and the activation energy was calculated [10,18]. Although these studies have produced good results, they do not directly reveal the

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formation process of tungsten carbide ceramics and its phase transformation. According to the W-C binary phase diagram [19] and the W-C-Fe system [20], there are metastable phases and polymorphism that exist, i.e., W_2C, WC, Fe_2W_2C, Fe_3W_3C and Fe_6W_6C [21,22]. Table 1 exhibits the crystalline structure parameters of these carbides. Particularly, with respect to W_2C, which involves the different lattice structures of β-W_2C, β'-W_2C, β''-W_2C, and ε-W_2C [19]. Nevertheless, science and technology are dedicated to revealing complex phenomena.

In the previous work [23], the WC-Fe layer on the iron substrate surface was produced via a combination of casting and solid-phase diffusion processes, and the growth kinetics for it was evaluated at 1085 °C, 1100 °C, and 1125 °C with extended treatment times. Only the WC phase was found in the WC-Fe layer, but the abovementioned other carbide phases were not involved and the microstructural evolution also was not presented. To understand the effect of the annealing temperature and time on the microstructure, the phase transformation, and the growth kinetics of tungsten carbide ceramics at the interface of iron and tungsten alloy, further investigation is needed. In the present paper, the WC, W_2C and Fe_2W_2C phases were obtained at 1100 °C, 1125 °C, 1150 °C annealing at short times (5, 10, 15, 20, 30 min) by ISS. Moreover, the microstructure of these carbides obtained and the growth kinetics of WC were investigated by X-ray diffraction, scanning electron microscopy and electron backscattered diffraction. This study will lead to a deeper understanding of the microstructure evolution of tungsten carbide ceramics at the interface of iron and tungsten.

2. Experimental details

2.1. Materials and preparation

High-quality tungsten wire (99.9%) with a length of 4 mm and a diameter of 2 mm was prepared to provide a W source for the reaction. The grey cast iron (Fe) (10 × 5 × 5 mm), as the bulk material, supplied the carbon (C), and its chemical compositions were determined using a spectrum analyser (EXF9600, Xifan, China) as follows, *w* (%) of 3.210 C, 0.045 S, 0.077 P, 1.320 Si, 1.050 Mn, 0.014 Cu, 0.240 Cr and 94.044 Fe. Several holes with 2-mm diameters and 4-mm depth were punched into the Fe bulk specimens. The tungsten wire and Fe matrix were ultrasonically cleaned in acetone for 15 min. The tungsten carbide ceramics at the interface of the iron and tungsten wire were prepared through diffusion reaction during the annealing process. The process parameters applied for the formation of tungsten carbides were implemented at 1100 °C, 1125 °C and 1150 °C for 5, 10, 15, 20, 30, and 60 min, respectively. Tungsten wires were inserted into the Fe matrix to form a precursor and the precursor was subsequently placed in a horizontal tube furnace with an Ar gas atmosphere at a flow rate of 5 ml/min. To avoid major thermomechanical stress between the Fe and tungsten carbides, the sample was removed from tube furnace and covered with quartz sand to cool the sample to room temperature after annealing.

2.2. Analysis methods

The surfaces of the samples were analysed to determine the microstructure and formation process of tungsten carbide ceramics. First, the samples were polished with SiC abrasive papers up to 1500 grit, etched with a 4% Nital, and ultrasonically cleaned in alcohol. With respect to the tungsten carbide, the microstructure was characterized by means of a scanning electron microscope (SEM, ZEISS, Germany) and the chemical compositions were evaluated by an energy dispersive spectral (EDS) analyser. In addition, the phase composition of carbides was analysed by means of X-ray diffraction (XRD) and electron backscattered diffraction (EBSD). An XRD-7000 (Shimadzu, Japan) with a 2θ of 20°–90° at a flat angle of 8° was used to determine the phase type. Additionally, the average thickness of the tungsten carbide layers was characterized by SEM images based on the results of five measurements.

3. Results and discussion

3.1. Phase and microstructure of the tungsten carbide ceramics

The phase compositions of tungsten carbides formed during isothermal annealing were determined by XRD and EBSD. At 1100 °C, the variation in phase composition of the samples as a function of the annealing time is shown in Fig. 1a and b, which indicates that the annealing time has an inconspicuous effect on the phase composition. Fig. 1a shows XRD results of the specimens annealed at 1100 °C for 5, 10, 15, 20 and 30 min. With the sample annealed at 1100 °C for 5 min, the XRD data just presented the W, α-Fe, and Fe_3C phases, and no tungsten carbide phase was observed. This result may be attributed to the low tungsten carbide content. As we all know, it is difficult for XRD to identify the type of phase when its content is less than 5%. Nevertheless, for the samples annealed at 1100 °C for 10, 15, 20 and 30 min, except the diffraction peaks of the W, α-Fe, and Fe_3C, the hexagonal structure of WC [13] was determined at 2θ of 35.641° and 73.104° (Fig. 1a), and the intensity of the corresponding peaks was enhanced gradually at the lattice planes of (100) and (111) with prolonged time, respectively. The result indicates that WC grains grow along the (100) and (111) planes. On the contrary, the intensity of the W diffraction peaks was weakened gradually at $2\theta$of 40.264° and 87.021°. Fig. 1b, c, and d show the phase variation as a function of the annealing temperatures at 1100 °C, 1125 °C and 1150 °C for 60 min, respectively. Fig. 1b exhibits WC diffraction peaks at 2θ of 35.641°, 73.104° and 75.477° corresponding with the (100), (111) and (200) reflections. The inset in Fig. 1b shows a magnified detail of 2θ in a range of 70°–78°. The quantity of the WC diffraction peaks for the sample at 1125 °C increased compared with that at 1100 °C, with the lattice planes of (101) and (201) appearing at 2θ of 48.296° and 84.068°, as shown in Fig. 1c. When the annealing temperature is elevated to 1150 °C, the XRD results containing the WC, α-Fe, and Fe_3C phases are shown in Fig. 1d. It is clear that the intensity and quantity of the WC peaks are enhanced remarkably and the W diffraction peaks disappear (Fig. 1d), indicating that the metal tungsten is consumed completely and the in situ reaction occurs fully. The obtained XRD

Table 1
Crystallographic parameters for some carbides in the W-Fe-C system.

Chemical formula	Structure	Space group	Lattice constants (A°)	References
WC	Hexagonal	P-6m2	a = b = 2.906, c = 2.837	[26]
W_2C	Hexagonal	P-3m1	a = b = 5.235, c = 4.777	[21]
Fe_2W_2C	Cubic	Fd-3s	a = b = c = 11.09	[22]
Fe_3W_3C	Cubic	Fd-3m	a = b = c = 11.02	[22]
Fe_6W_6C	Cubic	Fd-3m	a = b = c = 10.87	[22]