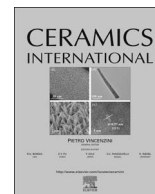




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Molten salt synthesis of continuous tungsten carbide coatings on graphite flakes

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ABSTRACT

Continuous tungsten carbide (WC) coatings were prepared on graphite flakes (G_f) by molten salt synthesis (MSS) technique using NaCl and KCl as reaction medium. The effect of reaction temperature, dwelling times and WO_3/G_f molar ratio on the compositions and morphologies of resultant samples was investigated, and the related formation mechanism for the coatings was also discussed. The results show that continuous WC coatings can be prepared at 1100 °C for 60 min with a WO_3/G_f molar ratio ranging from 1/15 to 1/5. These coatings exhibit homogeneous and crack free features, and their thickness increases with the increase of molar ratio. With the WO_3/G_f molar ratio below or beyond the above range, discontinuous WC coatings or $W/W_2C/WC$ flake-like particles without graphite are obtained, respectively. The varied compositions of the samples obtained with different WO_3/G_f molar ratio can be related to the detailed chemical reaction process between WO_3 and G_f in the molten salts. A “template-growth” mechanism is proposed to explain the formation of WC coatings in the MSS process.

1. Introduction

Because of the high thermal conductivity, low density, excellent self-lubricating ability and thermal shock resistance, graphite flakes (G_f) are extensively incorporated into other materials to manufacture various types of products, which have been widely applied in electronic packaging, metallurgy, advanced engineering, refractory industries, etc [1–5]. Unfortunately, the low oxidation resistance of G_f itself and the interface incompatibility between graphite and most materials negatively affect the performances of the products, and thus limit their further wider applications. To overcome these problems, several techniques and methods have been explored, such as surface functionalization [6], metal alloying [7] and coating techniques [8,9].

For the coating techniques, various types of materials (e.g. oxides and carbides) have been prepared on the surface of graphite. Zhang et al. [10] has used a sol-gel technique to form Al_2O_3/SiO_2 coating on the surface of graphite to improve water wettability and oxidation resistance. Yilmaz et al. [11] and Saberi et al. [12] have reported the coating of boehmitic alumina and $MgAl_2O_4$ spinel on the surface of G_f also by the sol-gel technique, respectively. However, the reported techniques suffer from several drawbacks, including high cost, difficulty

in making thick enough coatings, as well as the weak coating-substrate bonding. In addition to oxides, a few carbide coatings have also been synthesized on graphite. For example, Ono et al. [13] has tried to make SiC coatings on graphite particles via a high speed impact treatment technique. Unfortunately, the SiC grains were loosely attached to the graphite surfaces, and the resulting coatings were discontinuous and easily peeled off on prolonged mixing, which is insufficient for the promotion of oxidation resistance and other properties. Despite these disadvantages for the coating techniques summarized above, the findings obtained so far have given one important clue, i.e., how to economically prepare high quality (continuous, thickness-controllable, and strong bonded) coatings on graphite matrices especially for G_f is the key issue remain to be resolved.

Recently, a low temperature and relatively low cost molten salt synthesis (MSS) technique has been developed [14–17], which offers opportunity for synthesis of high quality carbide coatings (such as TiC and SiC) on various carbon substrates. Actually, Liu et al. [14] and Masoudifar et al. [18] have synthesized continuous TiC and discontinuous SiC coatings on the surface of G_f by MSS technique, respectively, and they found that the water wettability and dispersivity of G_f can be improved by these coatings. Comparing with TiC and SiC, WC has not

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only high thermal conductivity and electrical conductivity, but also high melting point and high chemical corrosion resistance [19,20]; more importantly, WC can wet most metals or alloys well [21–23]. These properties make WC a very attractive coating material for the modification of G_f . However, there are few reports on the synthesis of WC coatings on G_f , not to mention tailoring their continuity and thickness.

In this work, the MSS technique was used to synthesize WC coatings on G_f by reacting with WO_3 particles in molten NaCl-KCl based salts. The effect of reaction temperature, dwelling time and WO_3/G_f molar ratio on the composition, continuity and thickness of resultant coatings was studied, and the related synthesis mechanism was also discussed.

2. Experimental

2.1. Raw materials and sample preparation

Natural G_f (99.5 wt% purity; Shangdong Graphite Co. Ltd., China) and WO_3 particles (99 wt% purity; Sinopharm Chemical Reagent Co. Ltd., China) were used as the main raw materials, and their morphologies (secondary electron images, SEI) are illustrated in Fig. 1. Clearly, G_f particles display neat plate-like morphology with an average diameter of about 500 μm (Fig. 1a) and a mean thickness of about 25 μm (the inset of Fig. 1a). Fig. 1b shows that the as-received WO_3 particles are irregular with a mean particle size of 50 μm , and their surfaces seem relatively smooth (the inset of Fig. 1b). In addition, the salts used were NaCl powders (99.5 wt% purity; Sinopharm Chemical Reagent Co. Ltd., China) and KCl powders (99.5 wt% purity; Sinopharm Chemical Reagent Co. Ltd., China).

WC coatings were synthesized on G_f particles by MSS method. Firstly, pre-dried NaCl and KCl powders were mixed uniformly with a molar ratio of 1:1 using an agate mortar. Then, the mixture of WO_3 and G_f particles with a molar ratio ranging from 1/2.5 to 1/20 was combined with the NaCl-KCl based salts in the weight ratio of 1:30. The powder mixture was placed in an alumina crucible with a lid and then heat-treated at 950–1150 $^{\circ}\text{C}$ for different times under flowing argon in a tube furnace. After cooling to room temperature (cooling rate: 2 $^{\circ}\text{C}/\text{min}$), the solidified product in the crucible was washed with hot distilled water and filtered to remove the residual salts, which was repeated several times until no Cl⁻ was detected in the filtrate by an AgNO_3 solution. The retrieved products, a mixture of coated G_f and some impurities (unreacted WO_3 and/or particles detached from G_f), were oven-dried at 120 $^{\circ}\text{C}$ for 5 h. In order to characterize and utilize these coated G_f , it is necessary to separate them from the impurities, and this can be performed by sieving, considering their obvious dimensional difference (Fig. 1).

In order to study the dissolution of WO_3 in the molten salts and understand the MSS mechanism, WO_3 particles were also mixed uniformly with the equimolar NaCl-KCl based salts in the weight ratio of 1:30, and then heat-treated at 700–800 $^{\circ}\text{C}$ for 60 min under Argon

atmosphere using the same tube furnace. After removing the residual salts and drying, the compositions and morphologies of these retrieved particles were examined using the techniques described below (Section 2.2).

2.2. Sample characterization

Phase identification in the coated G_f was performed by a powder X-ray diffractometer (XRD, SHIMADZU XRD-7000, Japan), and the XRD spectra were recorded at 40 mA and 40 kV using Ni-filtered Cu K α radiation. The scan rate (2θ) was 8 $^{\circ}/\text{min}$ with a step size of 0.05 $^{\circ}$. The microstructure and the compositions of samples were examined by backscattered electron image (BEI) and SEI in a field emission scanning electron microscope (SEM, FEI Quanta 600, USA) equipped with an energy-dispersive spectroscopy (EDS) analyzer. Given that G_f particles tend to lie on top of each other naturally, the observation of their cross-sectional microstructure was performed by mounting the coated G_f in thermosetting resin, and then the plane that perpendicular to the alignment direction was observed after careful grinding and polishing.

3. Results and discussion

3.1. Effect of reaction temperature on the MSS

The XRD patterns of the coated G_f particles synthesized by using a WO_3/G_f molar ratio of 1/10 for 60 min at different temperatures are displayed in Fig. 2. As seen, the diffraction peaks of W are detected in the samples obtained at 950 $^{\circ}\text{C}$ and their intensity increases with increasing temperature, illustrating that WO_3 was gradually reduced to W by reacting with G_f at elevated temperature. After MSS at 1050 $^{\circ}\text{C}$, on one hand, the peaks of W disappear while those of WC appear, which indicates that the generated W phase has completely reacted with G_f to form WC; on the other hand, apart from WC peaks, the diffraction peaks of G_f still remain, indicating that part of G_f was involved in the reaction. On further increasing temperature from 1050 $^{\circ}\text{C}$ to 1150 $^{\circ}\text{C}$, no phase changes can be seen, but the WC peaks become higher and sharper gradually, stating a slight increase in its crystallinity and/or crystal size.

SEI of these coated G_f particles synthesized at different temperatures for 60 min is illustrated in Fig. 3. After MSS at 950 $^{\circ}\text{C}$, some bright depositions, although small in number, are observed on the surface of G_f particles (Fig. 3a), and the coverage extent of these depositions increases gradually with increasing temperature (Fig. 3b and c). With the temperature increasing to 1100 $^{\circ}\text{C}$ (Fig. 3d), the bright WC depositions, as identified by XRD analysis (Fig. 2), are fully covered on the surface of G_f and the high magnification SEM image (the inset of Fig. 3d) reveals that they are composed of many submicro-sized grains. Further increase the temperature to 1150 $^{\circ}\text{C}$ does not alter the continuity of the WC coatings on G_f (not shown). Obviously, these WC-coated G_f particles exhibit similar morphology and size to the

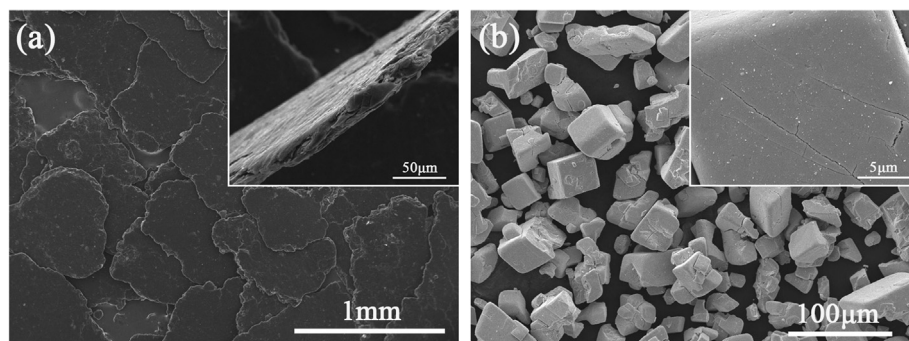


Fig. 1. SEI of the as-received (a) G_f and (b) WO_3 particles.

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