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Letter

In situ synthesis of TiC reinforced metal matrix composite (MMC) coating by self propagating high temperature synthesis (SHS)

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ABSTRACT

This paper reports a simple and energy saving method to prepare ceramic particulate reinforced MMC coating via SHS. By this method, TiC reinforced Cu/Ni based MMC coating was produced on a steel substrate. No pores or micro cracks were found in the coating, and fine TiC particles were uniformly distributed in the metal matrix. A strong metallurgical bonding was achieved at the interface between the MMC coating and the steel substrate.

1. Introduction

Ceramic particulate reinforced metal matrix composites coatings have attracted wide interest in recent years because of their unique comprehensive properties. Therefore, several techniques have been applied to fabricate MMC coating, including plasma spraying, laser cladding, arc welding and so on. Yuan et al. prepared WC-Co-based coatings containing solid lubricant Cu and MoS_2 on mild steel substrates by atmospheric plasma spraying [1]. Zhou and Zeng obtained WC-reinforced Fe matrix composite coatings by laser induction hybrid rapid cladding [2]. Buytoz obtained SiC reinforced MMC surface on AISI 304 stainless steel by TIG surface alloying [3]. In addition, Wu et al. produced Al/WC composite coatings in Al–12.6Si alloy by high energy milling [4]. However, several techniques were put forward to prepare MMC coatings, but it required complex preparation process and expensive equipment.

As an alternative approach, SHS has been recently reported to prepare ceramic particulate reinforced MMCs [5–9]. The SHS method does not need complex equipment and shows the advantage of low energy consumption, high time efficiency, and good interfacial bonding. The fabrication of MMC coatings by SHS, however, has rarely been reported. In this work, TiC reinforced Cu/Ni based MMC coating was in situ synthesized via SHS on a steel substrate. Both the microstructure of the MMC coating and the bonding state at the interface were examined.

2. Experimental

2.1. Materials

Two types of starting powders were prepared. The first one (type-I) was prepared by mixing commercial powders of Cu, Ti, and C, in order to produce a composite of (60 wt.% Cu + 40 wt.% TiC). The second one (type-II) was prepared by mixing powders of CuO, NiO, Al, Si, and B_2O_3, in order to produce a Cu/Ni alloy with the composition of 85 wt.% Cu + 15 wt.% Ni (using the following reactions of Eqs. (1)–(3)). Here, B_2O_3 was added as a slagging agent to facilitate the separation between alumina and metal melts product. Q235 steel with the dimension of 100 mm × 50 mm × 3 mm was used as the substrate material.

$$2Al + 3CuO \rightarrow 3Cu + Al_2O_3 \tag{1}$$

$$2Al + 3NiO \rightarrow 3Ni + Al_2O_3 \tag{2}$$

$$Si + 2CuO \rightarrow 2Cu + SiO_2 \tag{3}$$

2.2. Coating procedure

A schematic illustration of the fabrication of MMC coating by SHS is shown in Fig. 1. Double layers of reactant powders were placed on the steel substrate. The lower layer consisted of 5 g type-I powder, and the upper layer consisted of 50 g type-II powder. The powder compacts were surrounded by a sand mold. Some igniting agent, which can be ignited by match, was placed on the top of the type-II powder compact to trigger the aluminothermic reactions. The reactions happened quickly and lasted for only several seconds. Finally, a coating with a thickness of ~3 mm was produced on the steel substrate.

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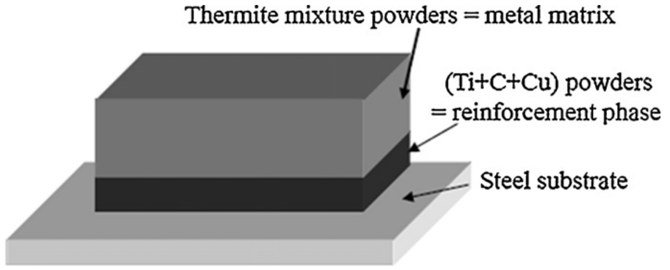

Fig. 1. Schematic of the fabricate MMC coating by SHS.

2.3. Characterizations

Samples were machined and then etched by a solution of $FeCl_3$ in absolute ethanol and HCl acid for microstructure observation by scanning electron microscope (SEM). X-ray diffraction (XRD) and Energy dispersive spectroscopy (EDS) was used for phase and chemical composition analysis respectively.

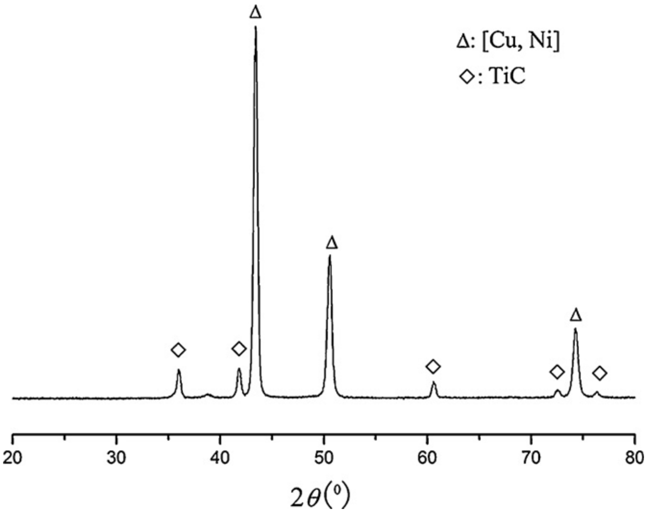

Fig. 2. XRD pattern of the as-synthesized coating.

3. Results and discussion

The XRD pattern of the as-prepared coating is shown in Fig. 2, which the diffraction peaks of Cu–Ni solid solution and TiC were found. The SEM micrograph of the coating is shown in Fig. 3. No pores or cracks were observed in the coating and interface. Fig. 3(b) shows a typical BSE image of the coating, where fine TiC particles (dark) were uniformly distributed in the metallic matrix (bright). EDS analysis also confirmed that the fine particles were TiC. The TiC particles showed a columnar morphology and an average size of <10 μm.

In addition, the amplified image (Fig. 4) of the metal matrix in the coating shows that dendritic structure has been formed. EDS analysis indicated that the dendrites were rich in nickel and iron, while the matrix surrounding the dendrites had a higher concentration of copper. The presence of Fe in the coating was caused by partial melting of the steel substrate during the reaction process. It also demonstrated that the interface between coating and steel substrate was metallurgical bonding. The difference in chemical composition between the dendrites and the matrix can be explained by the rapid solidification theory of metal.

For the novel coating route, the key point is to obtain high temperature metal melts conveniently, which could ignite the SHS reaction of Ti–C and fuse the reinforcement phase onto the substrate surface.

As we known, the term thermite reaction is used to describe a much broader class of exothermic reactions. There are a number of factors involved in the selection of a reducing agent for a particular oxide. The tendency for a metal to reduce an oxide depends on the free energy of formation of its oxide. Element Si as a common reducing agent shows negative Gibbs free energies of oxide formation over a wide temperature range. Goldschmidt used intermetallic reactants (Ca–Si, Ca–Al, and Mg–Si) instead of aluminium as reducing agents in order to form lower melting compounds [10]. In this work, we employed this approach by using Si partly instead of aluminium as reducing agents to lower the melting point of aluminium oxide. In addition, our previous study showed that adding some slagging medium composed of boron oxide into the thermites could facilitated the separation process of aluminium oxide product from molten metal [11]. The binary Al_2O_3–B_2O_3 equilibrium diagram shows that B_2O_3 can reduce the melting point of Al_2O_3 significantly by forming $Al_{18}B_4O_{33}$ or $Al_4B_2O_9$ phases with low melting points. Because of low melting points, those phases could rapidly separate from molten metal products and lift to the top owing to its lower density. Therefore, the pure molten metal

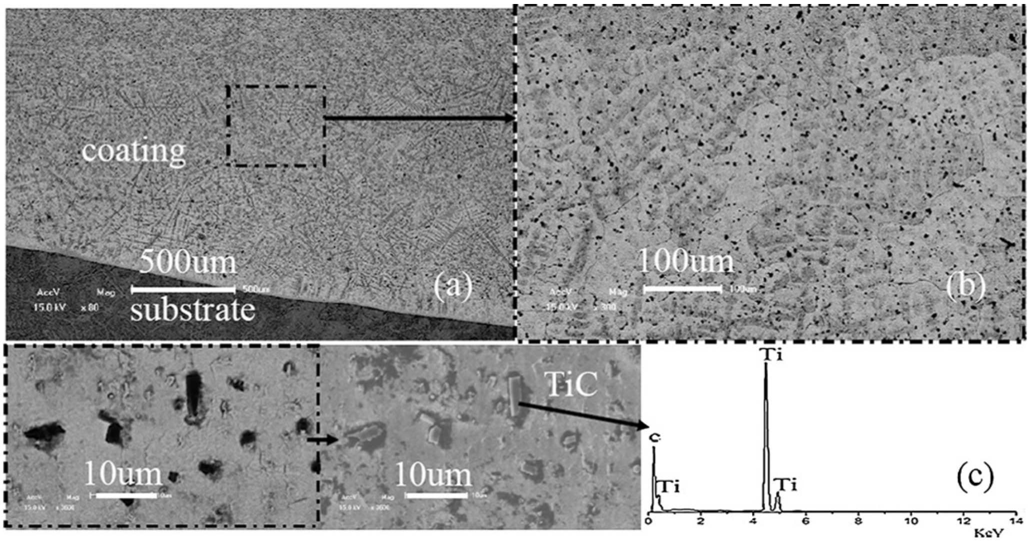

Fig. 3. SEM (a) and BSE (b) micrograph of the coating microstructure, SEM and EDS analysis (c) of dark phase in the coating.

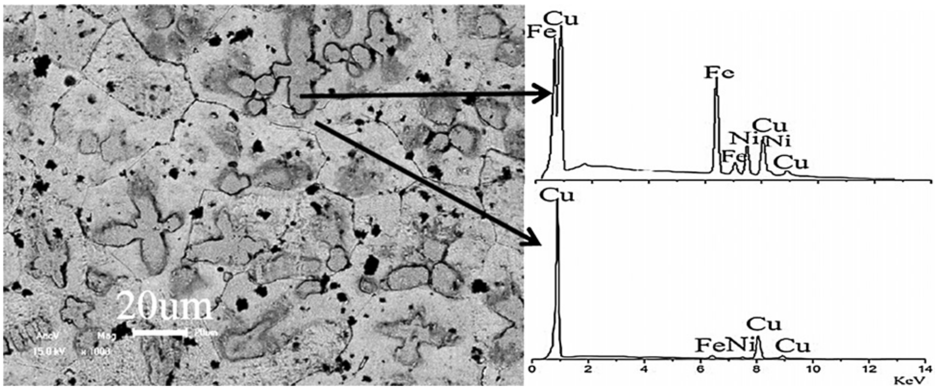

Fig. 4. BSE image of the metal matrix and EDS analysis of dendritic structure.

without aluminium oxide products could pour down and deposited on the lower layer powder compacts (type-I powder) and ignite the SHS reaction of Ti–C–Cu system.

It has been well studied to prepare TiC by SHS reaction from (Ti + C) powder mixture [12–14]. In the Ti–C system, the ignition temperature was generally close to the melting point of Ti, and can be lowered by adding another metallic powder such as Cu. Differential thermal analysis showed that the reaction initiated at around 960 °C which was the eutectic point for the melting of $CuTi_2$ and CuTi in Ti–C–Cu system [15]. The formation mechanism of TiC in the ternary system can be described as dissolution-precipitation, namely, Ti and C dissolve in the Cu melt which then precipitates out TiC upon cooling.

Therefore, a proposed mechanism and speculation of the formation of TiC reinforced Cu/Ni matrix coating follows. In present work, Cu started to melt initially upon the molten Cu/Ni metal depositing on the lower layer compacts. With increasing temperature, the Cu–Ti liquids formed via the diffusion reactions between the Cu and Ti. The unreacted Ti and C particles dissolved into the Cu–Ti liquids and led to the formation of the Cu–Ti–C ternary liquids; subsequently, TiC formed in the liquids. Then Ti and C particles continuously dissolved into the Cu–Ti–C liquid and TiC particulates gradually precipitated out of the saturated liquids.

4. Conclusions

A novel method to prepare MMC coatings via SHS was developed. The main aim was to obtain ceramic particulate reinforced metal matrix composites coatings employing a simple and energy-saving process.

An in situ synthesized TiC reinforced Cu/Ni based MMC coating was successfully produced on a steel substrate via this process. Fine (less than 10 μm) columnar morphology TiC particles were uniformly distributed in the metal matrix and no pores or microcracks were found in the coating. A strong metallurgical bonding was achieved at the interface between the MMC coating and the steel substrate. We believe that this method can be also applied to a large number of other SHS systems to obtain different MMC layers.

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