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Microstructure and tribological properties of laser-clad Ni–Cr/TiB_2 composite coatings on copper with the addition of CaF_2

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ABSTRACT

In this study, Ni–Cr/TiB_2 metal matrix composite (MMC) coatings with the addition of a little CaF_2 (2 wt.%) were successfully fabricated on a Cr–Zr–Cu alloy substrate by laser cladding process with powder mixtures of Ni, Cr, TiB_2 and CaF_2 as the precursor materials. The MMC coatings were free of defects and the interfacial substructure between the MMC coatings and the copper substrate was epitaxial, with excellent bonding by the strong metallurgical interface. The microstructure, phase and tribological properties were investigated by means of optical microscopy (OM), X-ray diffraction (XRD) and scanning electron microscopy (SEM), as well as dry sliding wear test. Results show that the influence of TiB_2 on the microstructure and tribological properties of the coatings was significant. The microstructure of the coatings was mainly composed of dendrites, cystiform-dendrites and particles. The dendritic microstructural features of the MMC coatings could be changed into particles by increasing TiB_2 to 20 wt.%. The laser-clad Ni–Cr/TiB_2 MMC coatings on copper with the addition of CaF_2 exhibited higher microhardness and better wear resistance than pure copper substrate. The highest microhardness was up to 946 $HV_{0.1}$ which was improved 8 times compared to the original substrate. The friction coefficient of the laser-clad Ni–Cr–20 wt.%TiB_2–2 wt.%CaF_2 coating was reduced significantly to about 0.24, and a relatively smooth wear surface could be observed.

1. Introduction

The high thermal and electrical conductivity of copper and its alloys makes them interesting materials for applications involving heat and electrical conduction, e.g., in continuous casting molds and electrical contacts [1,2]. However, due to the low slide wear resistance and electric erosive resistance of copper when subjected to severe conditions, its durability is reduced seriously. By using coating technologies, it is possible to overcome the difficulty of copper components, and to take the advantage of a longer service life of coatings for reduction of the total cost. Therefore, there is an increased interest to improve tribological properties of the actively cooled copper components through the application of surface coatings including electroplating [3], thermal spraying [4,5] and infiltration technique [6] developed on copper for continuous casting molds. Using these methods, although the wear resistance of copper can be raised to a certain degree, their practical application has been restricted greatly due to mechanical bonding between the coatings and Cu substrate. Fortunately, laser cladding technique is an effective means to achieve this goal. A good metallurgical bonding can be obtained between laser-clad coatings and substrate, without affecting or altering the properties of the bulk of the component. The most important one arises from the fact that laser cladding is a nonequilibrium method involving high cooling rates (10^3–10^8 Ks^{-1}) which produce metastable phases by exceeding the solid-solubility limit beyond the equilibrium phase diagram with an excellent metallurgical bond to the substrate. Therefore, it has become an alternative technique to conventional methods in order to produce large area coatings over metallic substrates [7].

Though laser cladding can be easily achieved for many metals such as steel [8,9], titanium alloy [10] and Ni-based superalloy [11], it is difficult to prepare defect-free coatings with large area on copper alloys, due to their good thermal conductivity and reflectivity to laser beam during laser processing. In the authors' previous work a high quality Co-Ni coating on copper substrate had been developed by Nd: YAG laser cladding [7]. In this study, we found that Ni was more compatible with copper substrate. Ni-based alloy laser-clad coatings fabricated on copper by Zhang et al. [12] also proved the point. However, it is limited to improving wear resistance of copper by laser cladding pure metal coatings. In recent years, literature on laser cladding shows increased interest in depositing metal matrix composite (MMC) coatings containing various volume fractions of ceramic particles like TiB_2, TiC, WC, etc. [13,14]. It has been reported that TiB_2 is the most inert, stiffest, hardest of all the borides, characterized by a high melting point, low specific weight, high mechanical strength, good wear resistance and excellent thermal and chemical stability up to 1700 °C [15]. MMC coatings containing TiB_2 present outstanding mechanical properties and wear resistance

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Table 1
Characteristics of Ni, Cr, CaF_2 and TiB_2 powders.

Reagent	Density (g/cm^3)	Particle size (μm)	Purity (%)	Source
Ni	8.90	74–150	99.50	Northeast Light Alloy Co., Ltd., China
Cr	7.14	74-150	99.0	Shanghai Sunrise Metal Co., Ltd., China
CaF_2	3.18	38–106	99.9	Tianjin Chemical Reagent Factory, China
TiB_2	4.52	74–100	99.5	Shanghai Sintec Ceramic Co., Ltd., China

because of good wettability of TiB2 to metal matrix. Furthermore, in contrast to other ceramic reinforcements, TiB_2 has the thermal and electrical conductivity. Therefore, these characteristics suggest that TiB_2 is a potential reinforcing material for wear applications.

Nevertheless, there are scarce reports about laser cladding TiB_2-containing MMC coatings on copper substrate at present [16–18]. The objective of this study was to fabricate abrasion-resistant TiB_2/Ni-based alloy MMC coatings on copper by laser cladding. In order to lower the melting point of the precursor, a little CaF_2 (2 wt.%) was added because CaF_2 is a fluxing medium in laser molten pool and increases the liquidity of melt [19]. Furthermore, CaF_2 has planes of perfect crystal cleavage in its crystal structure suggesting low shear strength [20] which may act as a solid lubricant to reduce abrasion. The focus of the present study was on characterizing microstructure and investigating tribological behaviors. It was expected that this route can provide a novel way for fabricating excellent wear resistant MMC coatings on copper and promote their commercial application in metallurgical and electrical equipment industries.

2. Experimental procedure

Experiments of laser cladding were conducted on a 400 W pulsed Nd:YAG laser ($\lambda = 1.064$ μm) material processing system with 3-axes computer numerical controlled (CNC) working station. A Gaussian pulse was adopted to obtain stable circular laser spot. The laser beam was focused by a focus lens with a focal length of 100 mm. The spot size of the laser beam was approximately 1.5 mm on copper surface. Though powder injection is commonly employed in laser surface modification, it was not selected in this study due to the high reflectivity of copper to laser. As the authors produced Co-based alloy coating on copper substrate by laser cladding in previous work [7], uniformly powder beds were applied to increase the laser energy absorptivity of the copper substrate surface.

The substrates of test coupons (50 mm × 30 mm × 10 mm) used for laser cladding were a copper alloy cut from a continuous casting mold, with the composition of Cu–0.9Cr–0.26Zr (wt.%). The copper coupons were surface machined and sand blasted to remove surface oxide before laser cladding. Commercially available Ni, Cr and TiB_2 powders were employed in this study. The characteristics of the powders used in the present study are listed in Table 1. The Ni-to-Cr mass ratio was 4:1 in Ni–Cr element mixture powder. The Ni–Cr element powder added a little CaF_2 (2 wt.%) were blended with 5, 10 and 20 wt.% TiB_2, respectively. Then, each blended precursor was milled in an agate tank for 4 h using a planetary ball mill at a rotating rate of 500 rpm. The ball-to-powder mass ratio used was 10:1. After ball-milling and drying, the powder was mixed with 5 wt.% acetyl-

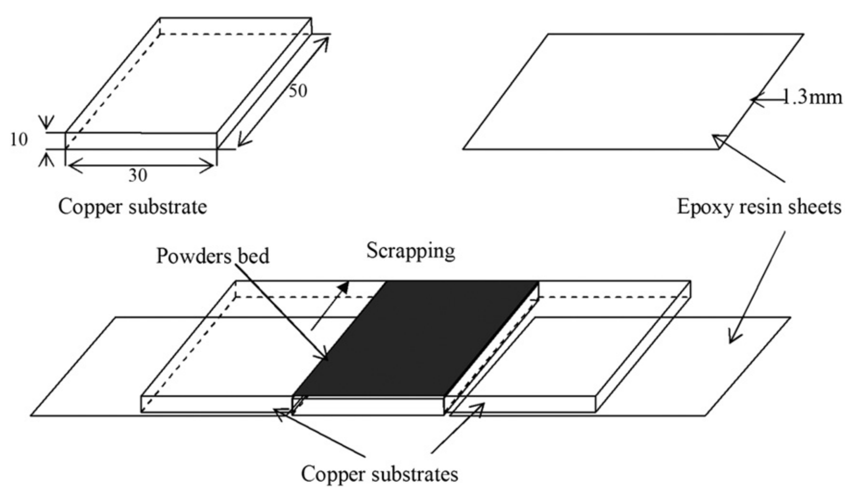

Fig. 1. Schematic diagram of preparation of powders and their preplacement on copper substrate.

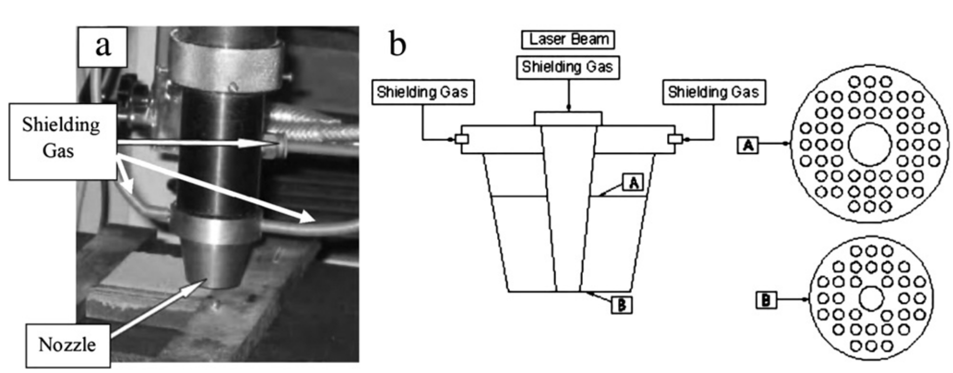

Fig. 2. Illustration of the renovated shielding gas apparatus: (a) experimental photo and (b) schematic diagram of the shield nozzle.