In-situ Dispersion of Titanium Boride on Copper by Laser Composite Surfacing for Improved Wear Resistance

J. DUTTA MAJUMDAR*a, B. RAMESH CHANDRA*b, D. BISWAS*d, B. L. MORDIKE**a, AND I. MANNA*a

*a Dept. of Met. & Mat. Engg., I. I. T., Kharagpur, W. B. - 721302, India
**a Institut for Werkstoffkunde und Werkstofftechnik, T. U. Clausthal, D-38678 Clausthal-Zellerfeld, Germany

The present study concerns the development of a hard in-situ titanium boride dispersed in a composite layer on a copper substrate with the objective of improving the wear resistance. Laser composite surfacing was carried out by melting the surface of a sand blasted commercially pure copper substrate using a continuous wave CO2 laser (with a beam diameter of 3.5 mm) and the simultaneous deposition of a mixture of K2TiF6 and KBF4 (in the weight ratio of 2:1) using an external feeder (at a feed rate of 4 g/min) and Ar as shroud. The process variables used in the present study were the laser power applied and the scan speed. Following the laser irradiation, a detailed characterisation of the composite layer was undertaken in terms of microstructure, composition and phases. Surface dependent mechanical properties such as micro-hardness and wear resistance were also evaluated in detail. Irradiation resulted in melting of the substrate, along with the delivered powder mixture, intermixing and rapid solidification. The microstructure of the composite layer consisted of uniformly dispersed titanium boride particles in a grain-refined copper matrix. The micro-hardness of the surface was improved threefold as compared to that of as-received copper substrate. There was a significant improvement in the wear resistance of the composite surfaced copper, as compared to that of the as-received copper. The mechanism of wear was investigated.

Key words: copper, titanium boride, laser, surface, wear, corrosion

*Corresponding Author: E-mail: jyotsna@metal.iitkgp.ernet.in
INTRODUCTION

Copper and its alloys have a potential scope for applications in electrical and petrochemical industries because of its high electrical and thermal conductivities [1]. However, the poor resistance to wear and erosion is of serious concern for prolonged use of components made of copper for articles such as switchgear [1, 2]. Metal matrix composites is a new class of material, which exhibits superior wear and erosion resistance, higher stiffness, hardness and strength at a lower density as compared to the matrix material [3]. However, they often lack sufficient toughness [3]. As wear is surface dependent degradation, it may be improved by the reinforcement of e.g. ceramic particles in the surface layer, which is indeed difficult to achieve by conventional surface treatment processes [4, 5]. On the other hand, a high power laser beam may be used to melt the metallic substrate and ceramic/inter-metallic particles may be dispersed in the molten metal to form a composite layer on the surface and may be termed laser composite surfacing [6]. The ability to deliver a large power / energy density ($10^3$ to $10^5$ W/cm$^2$), high heating/cooling rate ($10^3$ to $10^7$ K/s) and solidification speeds (up to 30 m/min) are the notable advantages associated with laser assisted composite surfacing [6–8]. Laser composite surfacing has been successfully attempted on Mg and its alloys to improve the wear resistance [9, 10]. Hu et al. [11] developed a layer of TiB$_2$ particles and also Al$_2$O$_3$ (Saffil) fibre to reinforce the metal matrix composite in commercial purity aluminium (CP-Al), 6061 and 8090 aluminium alloys, magnesium (We43), Stellite (Co-Cr-W), and commercially pure titanium (CP-Ti) substrates. In-situ composite formation involves synthesis of the composite during processing and the presence of a uniform distribution of reinforcement and a clean interface, which assists in the formation of a strong bond between the reinforcement and the metallic matrix [12]. In the past, laser surface alloying of Cu with Cr was achieved by pre-deposition of Cr on Cu by electro-deposition and subsequently, melting it using a continuous wave CO$_2$ laser. Laser surface alloying of Cu with Cr led to the formation of fine Cr-rich precipitates in the Cu matrix (with a supersaturated solid solution of Cr in Cu). Laser surface alloying led to a significant enhancement in wear and erosion corrosion both at room and elevated temperatures [13, 14]. However, composite surfacing of copper by the formation of in-situ titanium boride reinforcement has not been attempted so far.

In the present study, an attempt was made to develop in-situ titanium boride dispersed copper based metal matrix composite layer on the surface of a copper substrate to improve its wear resistance. Detailed studies on the microstructure, phases and composition of the composite surfaced region have been undertaken. Finally, the surface dependent mechanical properties such as micro-hardness and wear resistance have been evaluated in detail.
EXPERIMENTAL DETAILS

In the present investigation, commercially pure copper of dimension: 20 mm × 20 mm × 5 mm was chosen as substrate. The surfaces of the substrates were sand blasted prior to laser processing in order to remove oxide scale. Laser composite surfacing was carried out by melting the surface of the substrate using a 10 kW continuous wave CO₂ laser (with a beam diameter of 3.5 mm) and simultaneous deposition of a mixture of K₂TiF₆ and KBF₆ (in the weight ratio of 2:1) through an external feeder (at a feed rate of 4 g/min) with Ar as shroud. The process variables used for the present study were applied laser power and scan speed. The specimens were mounted on a CNC controlled X-Y stage which was moved at a speed of 100–1200 mm/min. A relative speed between the laser beam and the specimen was maintained to control the substrate-laser beam interaction time and a greater area of coverage. In order to achieve micro-structural and compositional homogeneity of the laser treated surface, a 25% overlap between successive melt tracks was followed. A large number of trials were undertaken using a wide range of laser power and scan speed combination to see the effect of laser parameters on the quality of composite layer. Table 1 summarizes the optimum laser parameters used for the formation of homogeneous and defect free microstructures. After laser processing, the microstructure of the composite layer (both the top surface and the cross section) was characterised by optical and scanning electron microscopy. A detailed analysis of the phase and composition was carried out by X-ray diffractometer and energy dispersive X-ray spectroscopy, respectively. The micro-hardness of the composite layer (both on the top surface and vertically in the cross sectional plane) was measured by a Vickers micro hardness tester using a 25 g applied load. Finally, the wear behaviour of the composite surfaced Cu was compared to that of the as-received copper using a Friction and Wear monitor unit (model no.: TR-208-M1) based on a pin on disc wear testing method with the specimen as disc and the diamond pyramid indenter (120°) as pin. During wear testing, the pin was allowed to slide over the disk with a 15 rpm wheel speed at an applied load of 1 kg. During wear testing, the cumulative depth of wear was measured as a function of time using Winducom 2003 software. The effect of load on the kinetics of wear was also studied.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Laser Parameter</th>
<th>Power (kW)</th>
<th>Scan speed (mm/min)</th>
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<tbody>
<tr>
<td>1</td>
<td></td>
<td>1.55</td>
<td>200–900</td>
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<tr>
<td>2</td>
<td></td>
<td>2</td>
<td>200–700</td>
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RESULT AND DISCUSSION

Characterization

A detailed characterisation of the composite layer in terms of microstructure, composition and phases was undertaken and correlated with the laser parameters to optimise the process parameters for laser composite surfacing. Figure 1 shows the optical micrograph of the cross section of the titanium boride laser composite produced with a power of 1.55 kW, scan speed of 500 mm/min and powder feed rate ($F_p$) of 4 g/min. The microstructure consists of finely dispersed titanium boride particles in a grain refined Cu matrix, which was confirmed by X-ray diffraction. The particle size was too small to be resolved by optical microscopy. In this regard it is relevant to mention that the depth of the composite layer was found to vary from 20 $\mu$m to 400 $\mu$m and increased with the increase in applied power density and decreased with increasing scan speed. Furthermore, the total depth of melting was found to be 500–700 $\mu$m. Hence, the particle penetration depth was much less than the total depth of melting. Figures 2(a, b) show the scanning electron micrographs of (a) the top surface and (b) the composite layer-substrate interface. In Figure 2 it can be seen that the microstructure of the composite layer consists of very finely dispersed...
titanium boride precipitates in a grain refined copper matrix. The average size of the particle was found to vary from 0.2 \( \mu m \) to 2 \( \mu m \). The average particle size and its distribution were however, found to vary with the laser parameters. It should be pointed out from Figure 2 that the interface
between the composite layer and substrate is continuous, adherent and defect free. Furthermore, the particles are distributed mainly along the grain boundaries but also within the grains. The particle size and its distribution were not found to vary significantly with depth. The uniform dispersion of the particles is attributed to rapid intermixing during laser melting and solidification leading to the formation of a uniform composition distribution all throughout. It may be noted further that the overall reaction showing the formation of titanium boride particles can be written as:

$$2K_2TiF_6(l) + 2KBF_6(l) + 9Cu(l) \rightarrow 2TiB \text{ (in alloy)} + 4KFCuF_2(l) + 2KF(l) + 5CuF_2(l)$$

Figures 3(a, b) show the microstructures of (a) the top surface and (b) the composite layer-substrate interface produced at a power of 2 KW and a scan speed of 200 mm/min. A close comparison between Figure 2(a) and Figure 3(a) reveals that the area fraction of coarse particles is marginally increased by the application of a higher energy i.e. a combination of higher power and lower scan speed. Also, the area fraction of the particles decreases when the laser beam has a higher energy density, Figure 3(a) vis-à-vis Figure 2(a). A decrease in the area fraction of particles with an increase in the applied energy is related to a greater depth of melting and hence, an increased dilution. The composite layer-substrate interface was however, continuous and defect-free as shown in Figure 3(b). From Figures 2 and 3 it may be pointed out that the particle size of the precipitates varies with the depth and laser parameters.

Figure 4 shows the average size and distribution of the particles on the surface of the laser composite surface with titanium boride at a power of 2 kW, 200 mm/min (bar chart 1) and 1.55 kW, scan speed of 500 mm/min (bar chart 2), respectively. Figure 4 shows that the particle size varies from 0.5 to 2.5 µm in both cases but the size distribution is random and varies with the laser parameters. However, it is apparent that the distribution of the finer size particles increases at a lower applied energy density and this is evident in the microstructures, Figure 3.

Figures 5(a, b) show the X-ray diffraction profiles of (a) the as-received and (b) the laser composite surface with titanium boride produced at a power of 1.55 kW and scan speed of 500 mm/min. A close comparison between Figure 5a and Figure 5b shows that there is a decrease in the relative volume fraction of the copper phase in the laser composite surface. The X-ray diffraction profile of the laser composite surface (cf. Figure 5b) also confirms the presence of titanium boride only (TiB). Hence, it may be concluded that the particles shown in Figures 2 and 3 are titanium boride (TiB) only. A detailed X-ray mapping was conducted to confirm the nature of the particles. Figures 6 (a–c) show the distribution of (b) titanium and
FIGURE 3
Scanning electron micrographs of the (a) top surface and (b) solid-liquid interface of laser composite surfaced Cu with titanium boride lased with a power of 2 KW and scan speed of 200 mm/min.
EVALUATION OF MECHANICAL PROPERTIES

The influence of laser composite surfacing on the mechanical properties are to be discussed, i.e. the micro-hardness and wear resistance.

Figure 7 shows the micro-hardness profiles with increasing depth from the surface of the laser composite surface. The laser power was 2 kW, 700 mm/min (plot 1), 2 kW, 900 mm/min (plot 2) and 1.55 kW, scan speed of 700 mm/min (plot 3), respectively. The micro-hardness of the composite layer is increased to 80–100 VHN compared to 65 VHN of the as-received Cu. Figure 7 shows that the micro-hardness is a maximum on the surface and decreases as the depth from the surface increases. The variation of micro-hardness with depth is attributed to the absence of titanium boride precipitates beyond a certain depth. However, due to the grain refinement in the melted region, the micro-hardness was improved in the melted zone beyond the composite region. Moreover, the average micro-hardness of the composite layer was found to vary with the process parameters. It was observed that laser processing at an increased power
FIGURE 5
X-ray diffraction profiles of (a) as-received and (b) laser composite surface on Cu with titanium boride with a power of 1.55 kW and scan speed of 500 mm/min.
FIGURE 6
X-ray mapping of the (a) laser composite surface on copper with titanium boride (with a power of 1.55 kW and scan speed of 500 mm/min) showing the distribution of (b) Ti and (c) Cu of the composite.
The effect of the scan speed on the micro-hardness was not so marked as the power was, but nevertheless increasing the scan speed increased the micro-hardness of the composite layer marginally (curve 2 vis-à-vis curve 1). The increase in micro-hardness of the composite layer with increasing scan speed and a decrease power is attributed to the increased area fraction of the particles. Hence, it may be concluded that the mechanism of hardening is mainly due to the dispersion of titanium boride particles in the matrix along with a marginal influence of grain refinement. The gradual change in micro-hardness with depth is beneficial as it avoids a sharp interface and reduces mismatch at the interface.

Figure 8 shows the change in cumulative wear loss in terms of the depth of wear as a function of time for the as received copper and the laser composite surface produced at a power of 1.55 kW and scan speed of 700 mm/min using a friction and wear monitor unit with an applied load of 1 kg. Figure 8 shows that the rate of wear is significantly higher in the as-received Cu than the composite surface. In both cases, wear increases with time for both the as-received and laser composite surface up to 1000 s...
Variation of wear loss (in terms of depth of wear) as a function of time for the as-received Cu and the laser composite surface on Cu with TiB (power of 1.55 kW and scan speed of 700 mm/min).

following which it reaches a constant value. The wear resistance of the composite layer increased with increasing micro-hardness of the composite layer. Hence, it may be concluded that the improved wear resistance of the laser composite surface is attributed to the improved micro-hardness of the composite layer due to grain refinement and precipitation of fine and hard titanium boride particles in the matrix. A detailed study of the microstructure of the debris was undertaken using a scanning electron microscopy to order to understand the mechanism of wear. Figures 9(a, b) show the scanning electron micrographs of the worn surfaces of as-received copper showing the (a) wear track and (b) higher magnification view of (a) against the diamond indenter at an applied load of 1 kg, applied rpm of 15 and 30 min. of test duration. In Figure 9 it is evident that the wear is predominantly abrasive in nature. Furthermore, there is evidence of fragmentation of the worn zone on the copper surface, along with a scratch mark as evidence that the mode of wear was high stress abrasion. Figures 10(a, b) show scanning electron micrographs of the worn surfaces of the laser composite surface produced at a power of 1.55 kW, scan speed of 700 mm/min showing (a) the wear track and (b) higher magnification view of (a) against diamond indenter at an applied load of 1 kg, applied rpm of 15 and 30 min. of test duration. A comparison of Figures 9 (a) and 10 (a) shows that the wear track width is significantly higher in the as-received copper compared to that of the composite surface. Fragmentation of material from the surface was not observed in the worn surface of the laser composite surface. Hence,
FIGURE 9
Scanning electron micrographs of the worn surfaces of the as-received copper showing the (a) wear track and (b) higher magnification of (a) against a diamond indenter at an applied load of 1 kg, applied rpm of 15 and 30 min.
FIGURE 10
Scanning electron micrographs of the worn surfaces of the laser composite surface on Cu with TiB produced at a power of 1.55 kW, scan speed of 700 mm/min showing (a) the wear track and (b) higher magnification view of (a) against a diamond indenter at an applied load of 1 kg, applied rpm of 15 and 30 min. of test duration.
In the present study, a composite layer of titanium boride (TiB) dispersed Cu-based metal matrix composite has been produced on the surface of a commercially pure Cu using laser composite surfacing. The following conclusions may be drawn from the detailed investigation.

1. The optimum processing regions for formation of a defect free and homogeneous composite layer were: power range of 1.55–2.0 kW, scan speed range of 200–900 mm/min and powder feed rate of 4 g/min.
2. Laser composite surfacing leads to dispersion of fine titanium boride dispersed (TiB) particles in a grain refined Cu-matrix. The area fraction of particles was found to increase with decreasing applied power and increasing scan speed. The area fraction of particles was almost uniform throughout the composite layer.
3. An improvement of the average micro-hardness, 85 to 100 VHN, was achieved in the laser composite surface as compared to that of the as-received copper, 65 VHN, a maximum improvement was observed for the sample produced with a power of 2.0 kW and scan speed of 700 mm/min.
4. A significant improvement in the wear resistance of twice was achieved in the laser composite surface as compared to that of the as-received Cu. The improved wear resistance is attributed to the increased hardness of the surface.
5. The mechanism of wear is mainly high stress abrasive in the as-received Cu. However, it is mainly abrasive with some fretting wear at very low magnitudes in the laser composite surface with TiB.

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