

# Enhancement of wear and corrosion resistance of metal–matrix composites by laser coatings

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A novel technique based on laser-induced chemical reduction of metal salts has been developed to produce surface coatings on metal–matrix composites (MMCs). The substrate is predeposited with a paste, containing concentrated salts of the elements to be coated along with a thickening agent, and then subjected to high power laser radiation. The rise in surface temperature during laser irradiation led to the decomposition of salts to their native metals. The combination of metal and metalloid elements in the reaction zone forms an amorphous layer due to the specific chemical ratio and rapid cooling rate. The thickness of the coatings obtained were of the order of 50–100  $\mu\text{m}$ . The coatings exhibited amorphous and microcrystalline structures, possessed hardness in the range of 300–1700  $H_V$  (substrate hardness 80–90  $H_V$ ), had superior sliding wear resistance and excellent corrosion resistance. The advantages of this process include the formation of complex coatings on MMCs by a simple, versatile technique which does not require any vacuum or inert atmosphere.

## 1. Introduction

Metal–matrix composites (MMCs) are emerging as the most versatile materials for advanced structural, automotive, aviation and aerospace applications. MMCs consist of a metal matrix, especially one with a low density, and a ceramic reinforcement, in various forms, such as whiskers, particulates or fibres. Current research efforts have involved developing aluminium, copper, magnesium and titanium based MMCs, but much of the emphasis has centred on developing aluminium-based composites. Reinforcements include graphite (Gr), silicon carbide (SiC), titanium carbide (TiC), tungsten (W), boron (B), titanium diboride ( $\text{TiB}_2$ ) or aluminium oxide ( $\text{Al}_2\text{O}_3$ ). MMCs are currently produced by four methods: diffusion bonding, conventional casting, powder metallurgy and squeeze casting, with the last two most commonly being employed [1].

Due to their high strength-to-weight ratio, high toughness and formability, MMCs have been investigated for use in antenna and aircraft support structures, torpedo and automobile engine pistons, aircraft vertical tail fins, and initial guidance and precision optical systems [2]. The potential application of MMCs in aero-engines and automotive applications have been reviewed by Wei [3] and Rohatgi [4], respectively. However, because of their unique combination of matrix and reinforcement, MMCs used in these applications are prone to corrosion, oxidation, erosion and wear. In order to improve their applicability it is essential to develop methods to protect them from

environmental and service degradation. One of the most conventional methods of improving the service performance of materials is by surface coatings. These coatings provide a physical barrier between the metal and the environment thus inhibiting the dissolution rate due to corrosion, enhancing oxidation resistance and, in addition, improving the wear resistance also. Trzaskoma [5] and Aylor [6] reviewed various coatings available for improving the corrosion resistance of MMCs. Although coating techniques such as chemical vapour deposition may be used to deposit protective coatings, the need for a vacuum will not permit these techniques to be used on large scale structures. Other methods, such as electroless plating, are tedious and not versatile. Hence, an innovative process is required to deposit protective coatings for composite structures without complexity. A laser glazing method may be effective in depositing amorphous coatings on composite surfaces and thereby provide the required protection. In the present investigation, the laser glazing technique has been extended to form metallic glass coatings on MMCs to enhance their corrosion, oxidation and wear resistance for aerospace, automobile and space applications.

## 2. Background

### 2.1. Amorphous coatings

Amorphous or glassy metals are single-phase alloys with a short-range order of atoms, which can be

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produced by rapid solidification of certain metal-metalloid or metal-metal melts. These supercooled glassy metals possess a remarkable combination of properties as a result of their unusual atomic structures. Such properties include: strength, hardness, ductility, toughness, corrosion resistance, electrical resistivity and magnetic permeability [7].

Glassy alloys can be produced from two or more transition metals, for example Cu-Zr, Ni-Nb, Ti-Be, Ca-Mg with 50:50 in composition. In the metal-metalloid group, typical glass forming compositions are 80 at % late transition metals, such as Fe, Co, Ni, Pd, Au and 20% metalloids, such as B, C, Si, P and Ge [8].

Due to the need for extremely rapid quench rates, glassy metals are often produced in the form of ribbons, wires and filaments [9]. Melt spinning is the usual method of producing glassy metals, yielding 20–60  $\mu\text{m}$  thick, 1–20 mm wide, ribbons. Another technique used to form glassy metals involves growth from the vapour phase, such as sputtering, or from a liquid phase, such as electroless deposition or electrodeposition. By virtue of their higher effective cooling rates, these techniques allow the formation of glassy metal that cannot be produced by splat quenching.

## 2.2. Laser surface modification processes

Lasers are increasingly being used in many surface engineering applications. The emergence of the laser as a tool for materials development and/or processing can be attributed to its characteristics, such as localized heat source, inertialess beam, highly controllable power density, short interaction time and chemical cleanliness. The variations in laser power density and interaction time have already resulted in several materials processing operations, such as transformation hardening, surface alloying, surface cladding and laser glazing [10].

The laser glazing process consists of melting a localized thin surface layer in intimate contact with a cold, solid substrate using a laser beam of high power density ( $10^5$ – $10^8$   $\text{W cm}^{-2}$ ) and a short pulse time ( $10^{-5}$ – $10^{-8}$  s). Rapid surface melting occurs in a time during which little thermal energy penetrates into the base material. This leads to the development of extremely high thermal gradients, which promote rapid solidification of the metal [11]. Cooling rates of the order of  $10^6$ – $10^8$   $^\circ\text{C s}^{-1}$  can be achieved which result in metastable microstructures with epitaxial growth. Solidification starts at the melt layer/substrate interface, and progresses towards the surface with continued cooling. The interface remains in an equilibrium state, while the material above it solidifies dendritically at a high quench rate. In special cases, amorphous solidification can occur with the suppression of crystallization.

## 3. Experimental details

### 3.1. Specification of substrates

The substrates used in this investigation were aluminium-based metal matrix composites (MMCs) rein-

forced with silicon carbide particles. The samples were sand cast Duralcan F3A. 10S and Duralcan F3A. 20S (general purpose composites), which contained 10 and 20 vol % silicon carbide particles, respectively. The discontinuous particles ranged in size from 15 to 50  $\mu\text{m}$ .

The nominal composition of matrix (A356) was 7 Si, 0.2 Fe, 0.20 Cu, 0.10 Mn, 0.35 Mg, 0.10 Zn, 0.20 Ti, balance aluminium (all in wt. %). Samples with dimensions of 15  $\times$  40  $\times$  6 mm were mechanically polished to a random finish with 320 grit SiC paper. The samples were then cleaned thoroughly with water and with methanol prior to laser treatment.

### 3.2. Laser coating process

In the present investigation, laser-induced chemical reduction of metal salts was used to form amorphous coatings. This method is based on the earlier work by Pons et al. [12], who reported the formation of Fe-Ni, Ti-Ni, and Fe-Ni-Cr surface alloys on mild steel and titanium substrates. Laser-induced heating has also been used in direct-write metallization on quartz or silicon for microelectronic applications [13, 14].

In this method, the substrate is first covered with a layer containing concentrated salts of the elements to be coated along with a thickening agent, such as agar, followed by laser irradiation. The rise in surface temperatures during laser treatment will lead to decomposition of the salts to their native metals. These metals will be dissolved into the melted substrate and form amorphous layers, due to the chemical composition and rapid cooling rate which is typical of the laser glazing process. Initial experiments were conducted by applying precursors of nickel, cobalt, chromium and phosphorous. Phosphorous was used due to its well established capability in enhancing the formation of glassy metals. The selected metal salts were nickel formate (Ni), cobalt acetate (Co), chromium chloride (Cr) and phosphorous oxide (P). The compositions of metal salts selected in the study have the capability of forming glassy structures. The chemical formulae, along with their weight percentages of elemental metal contents, are listed in Table I. The preparation process involved mixing the metal salts, in the given proportion, with water. A thickening agent (5–10 wt % agar-agar gum) was used to enhance the viscosity of the solution. The solution was heated at 100–120  $^\circ\text{C}$  for 10–15 min to evaporate water. The resulting thick paste was applied uniformly on the sample with a

TABLE I Composition of metal salts used in the study

Chemical name	Formula	Formula weight	(Wt. %) Metal
Nickel formate	$\text{Ni}(\text{CHO}_2)_2 \cdot 2\text{H}_2\text{O}$	184.71	31.70 (Ni)
Cobalt acetate	$\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	249.08	23.66 (Co)
Chromium chloride	$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$	266.45	19.51 (Cr)
Phosphorous pentoxide	$\text{P}_2\text{O}_5$	141.94	43.68 (P)

spatula. The thickness of the coating was of the order of 3–5 mm. In the second method, the salts were dissolved in methanol. The mixture was deposited on the substrate and heated to 60–80 °C for a few minutes and allowed to cool to obtain a solid precursor layer. Results indicate that amorphous layers were produced better by using water as the solvent. The substrates covered with a thick layer of metal salt precursors were irradiated with: (i) Nd:YAG laser with powers of 50 continuous wave (WCW) and 400 W (pulsed), (ii) excimer laser (ArF) with an average power of 4 W, and (iii) CO<sub>2</sub> lasers with powers ranging from 250–1250 W under varying process conditions. The specifications of the lasers used in the investigation are listed in Table II. After laser irradiation, the samples were thoroughly cleaned with water to remove the untreated precursors and resultant organic residues. The effect of laser power and specimen scanning rate on the capability of forming metallic glass layers was investigated.

Due to success with the CO<sub>2</sub> laser, further experiments were carried out using a 1.5 kW (nominal) CO<sub>2</sub> laser. The CO<sub>2</sub> laser yielded better results because of its high power, better beam profile and small divergence. It should be added that a low-divergence type laser, such as CO<sub>2</sub>, is ideal for accurate and reproducible results due to its high power and better beam quality.

A typical experimental set-up for the CO<sub>2</sub> laser is shown in Fig. 1. The Gaussian beam from the laser was made to oscillate bidirectionally by means of wobble rotation of a mirror, and then focused through a lens to form an elliptical profile. The size of the ellipse may be increased by reducing the  $\theta$  angle and thereby providing increased coverage rate. The purpose of oscillating a focused Gaussian beam was to enhance the coverage zone. Typical widths of laser glazed zones, depending on the focal length of the lens, were from 5 to 10 mm. The frequency of oscillation was made constant in this study and was equal to 1000 r.p.m.

Laser glazing experiments were conducted using three different focal length lenses: 63, 127 and 188 mm, and the best results were obtained with the 127 mm focal length lens. The scan rate of the laser beam is an important parameter and determines the interaction time of the laser beam. The scan rates were varied from 4 to 254 mm s<sup>-1</sup>. For the oscillating beam set-up,

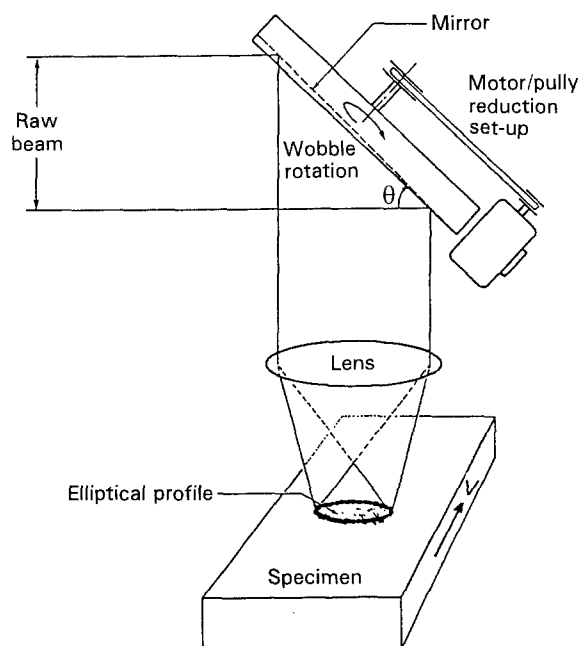


Figure 1 Experimental set-up for laser glazing process.

the scan rate was held less than 40 mm s<sup>-1</sup> because the frequency of oscillation (1000 r.p.m.) was not high enough to allow continuous, uniform coverage. An argon shield gas was used to protect the lens during laser glazing.

In the oscillating Gaussian beam set-up, the laser glazed width per scan was about 5 mm when the 127 mm focal length lens was used. Multiple, overlapping scans were carried out to increase the width. For characterization and analysis purposes, a total of three scans with an overlapping of about 30% for each sample were performed. For corrosion and wear test samples, a total of 20 scans were carried out. Fig. 2 shows the top view and transverse section of a multiple laser scan sample. There is 50% overlap in each of the scans. It is to be noted that tempering always occurs in multiple laser scans. In amorphous coatings the tempering results in crystallized zones.

### 3.3. Friction and wear testing

Friction and wear tests were conducted using the well known pin-on-disc test rig. The sliding system consisted of laser-coated Al–SiC (disc) and hardened 52100 steel pin (6 mm diameter, 25 mm long). The wear test parameters are given in Table III. No lubricant was added and the humidity was controlled to 60%. The additive weight loss of the disc was measured to determine wear, using a precision balance with an accuracy of 10<sup>-5</sup> g. Wear tests were also carried out using 6061–Al alloy and uncoated Al–SiC as discs for comparison purposes.

### 3.4. Evaluation of corrosion resistance by anodic potential test

For corrosion testing, lacquer was applied on all sides of the sample except on the laser-treated face, leaving an exposed area of about 13 225 mm<sup>2</sup> for electrochemical testing. The electrolyte used was aerated

TABLE II Specifications of the lasers used in the study

	Nd:YAG (pulsed)	Nd:YAG (CW)	CO <sub>2</sub> (CW/ pulsed)	Excimer ArF (pulsed)
Average power (kW)	0.4	0.1	1.5	0.05
Wavelength (nm)	1060	1060	10600	193
Peak power (kW)	12	0.1	5	20000
Pulse time	ms	–	ms	ns
Repetition rate (Hz)	1–200	–	1–100	1–100
Beam quality	Multimode	Multimode	Gaussian	Multimode

(open to air) 0.1 M NaCl. The experimental procedure involved recording open-circuit potential with the time of immersion, and monitoring current-potential relationships using the potentiodynamic polarization technique. The samples were immersed in electrolyte until a steady open-circuit potential ( $E_{\text{corr}}$ ) was recorded (approximately for 1 h). After this time the potential was increased at a rate of  $0.5 \text{ mV s}^{-1}$ . Potentiodynamic polarization curves were recorded with an EG & G PAR Model 273 Potentiostat/Galvanostat controlled by an external microcomputer.

## 4. Results and discussion

### 4.1. Metallography and compositional analysis

The laser-coated specimens were sectioned perpendicular to the scan direction, mounted in epoxy, mechanically polished and etched for 8–12 s in Keller's etchant. The specimens were then examined by optical and scanning electron microscopy. It was observed that the use of Nd:YAG at 50 W (CW) and 400 W (pulsed), excimer laser at 4 W and CO<sub>2</sub> laser at 250 W did not cause any significant reduction of metal salt precursors. This may be due to the low temperatures

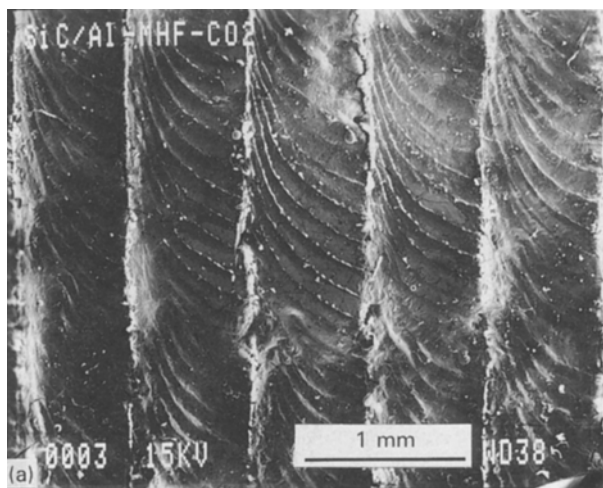


TABLE III Sliding wear test conditions and parameters

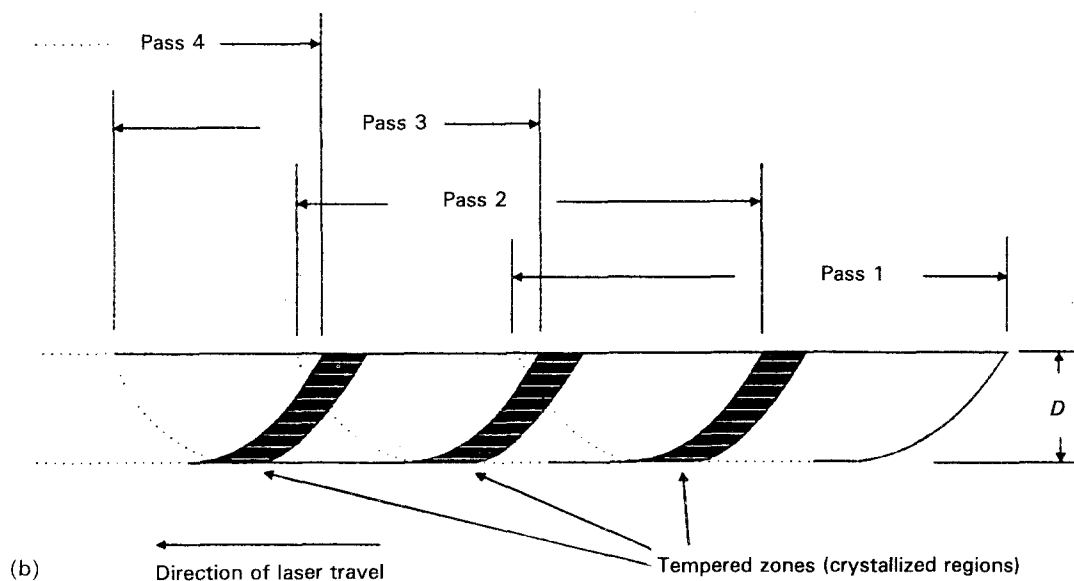
Pin	Hardened 52100 steel	60–64 Rc
Disc	Al-SiC substrate	80–90 H <sub>v</sub>
	Laser coated Al-SiC	300–1700 H <sub>v</sub>
	6061-T6 aluminium	100–110 H <sub>v</sub>
Load	10 N	
Velocity	$0.183 \text{ ms}^{-1}$	
Diameter of track	10 mm	
Sliding time	$\leq 5 \text{ h}$	
Temperature	Ambient	

generated during laser irradiation, which are insufficient to decompose the metal salts.

Only use of the CO<sub>2</sub> laser at higher powers (500 W and above) showed the formation of amorphous-like layers on the surface, as shown in Fig. 3. Scanning electron microscopical examination shows the coating thickness to be of the order of 100  $\mu\text{m}$ . Examination at higher magnifications did not reveal any crystalline structural features, leading to the possibility that the coating is amorphous.

Metallographic analysis showed evidence of an amorphous-like coating in those samples prepared with metal salt precursors of Ni, Co and B. Fig. 4 shows the formation of an amorphous-like coating on those samples glazed at a laser power of 1500 W. Analysis at various locations on the samples confirmed the nature of coatings to be consistently amorphous-like, with coating thickness ranging from 50–70  $\mu\text{m}$ . Microstructural examination of coatings, even at higher magnification, did not reveal any specific structural features. WDAX showed the presence of Ni, Co, Si and Al in the coating. The presence of Al and Si in the coating indicates the possibility of vigorous surface reaction between the metal salts and the composite substrate. There was no evidence of cracks, or porosity, in laser glazed layers.

Figure 2 (a) Scanning electron micrograph showing the top view of laser glazed sample, magnification  $\times 30$ . (b) Schematic showing the transverse section of multiple overlapping laser scans.



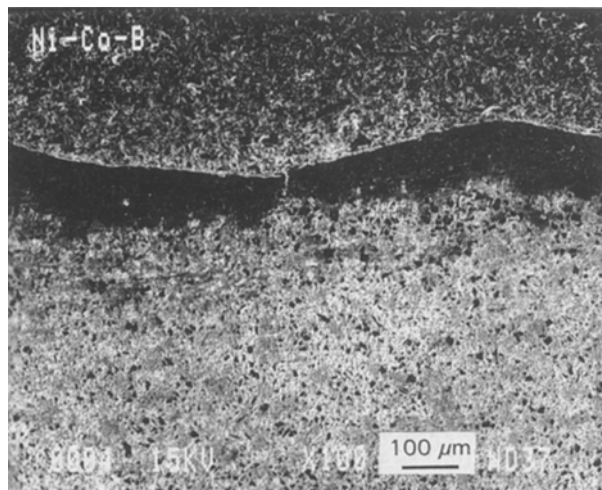


Figure 3 Scanning electron micrograph of laser glazed Al-SiC predeposited with nickel, cobalt and boron showing amorphous-like coating. Magnification  $\times 100$ .

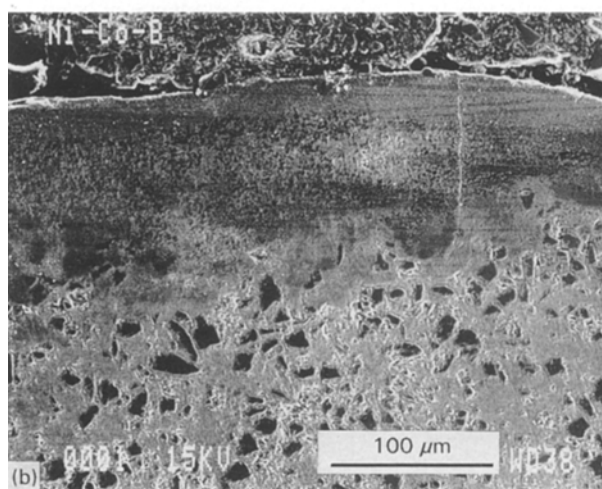
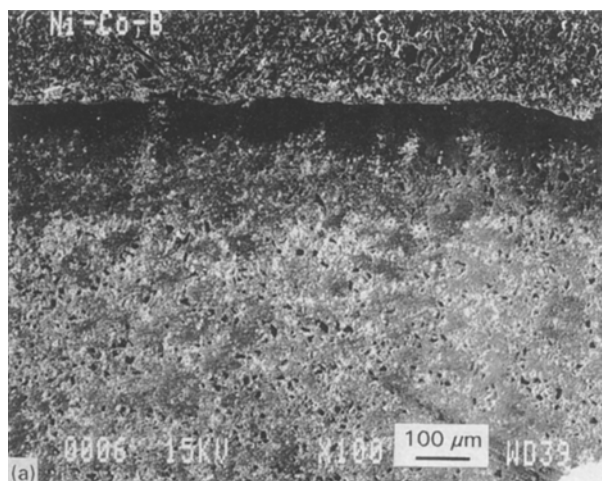


Figure 4 Scanning electron micrographs of laser glazed Al-SiC predeposited with salt precursors of Ni, Co and B (laser power 1500 W) showing the uniform glassy-like layers. Magnification: (a)  $\times 100$ , (b)  $\times 300$ .

#### 4.2. X-ray diffraction analysis

Structural and compositional analyses of the laser-processed samples were analysed by the X-ray diffraction method using  $\text{CuK}\alpha$  radiation. The X-ray dif-

fraction patterns were obtained using a Siemens D500/SRS 200. The X-ray diffraction pattern of the Al-SiC composite substrate showed sharp peaks associated with Al, Si and SiC. The X-ray diffractograms of laser glazed Ni-Co-B and Ni-Cr-Co-B coatings exhibited both diffused and sharp peaks characteristic of amorphous and crystalline structures. The crystalline phases were identified to be intermetallics that included nickel cobalt chromium (NiCoCr), aluminium carbide ( $\text{Al}_4\text{C}_3$ ) and aluminium cobalt ( $\text{Co}_2\text{Al}_9$ ) in addition to Al, Si and SiC phases. Intermetallic NiCoCr usually forms under rapid solidification conditions. The X-ray patterns exhibited broader and diffused peaks, indicating that the coating consisted of a mixture of amorphous and crystalline regions. Note that the depth of X-ray penetration is larger than that of the coating thickness.

#### 4.3. Microhardness evaluation

Microhardness tests were conducted using a Vickers diamond pyramid indenter at a load of 500 g. The hardness of laser glazed layers was substantially higher than the substrate. The hardness of surface layers varied as a function of scan rate. Table IV provides the hardness and glazed depth (coating thickness) of Ni-Cr-Co-B coatings. The hardness of the overlapping zones (250–300  $\text{H}_\text{V}$ ) was lower than the single scan zone (400  $\text{H}_\text{V}$ ). The hardness increased with decreasing scan rate. The sample processed at a low scan rate,  $17 \text{ mm s}^{-1}$ , consisted of soft and hard regions with hardness ranging from 300 to 1700  $\text{H}_\text{V}$ . High hardness regions did not exhibit any crystalline features.

#### 4.4. Tribological properties

Fig. 5 provides the weight loss as a function of sliding time for Al-SiC, laser-coated Al-SiC with Ni-Cr-Co-B and 6061-T6 aluminium. It is seen that the uncoated Al-SiC wears out linearly with time and also has excessive wear when compared to laser-coated Al-SiC. The laser-coated sample exhibited a higher wear rate initially, due to the presence of loose oxides and surface roughness. After “running-in” wear, the wear rate became negligible. Such wear behaviour is not observed in 6061-T6 aluminium and uncoated Al-SiC samples. This clearly indicates that the laser coating has a superior capability to enhance wear resistance. Friction data plotted in Fig. 6, show that steady-state friction for the laser-coated sample is

TABLE IV Microhardness data of Ni-Cr-Co-B laser coatings

Scan rate ( $\text{mm s}^{-1}$ )	Average coating thickness ( $\mu$ )	Hardness readings ( $\text{H}_\text{V}$ )
42	30	110 <sup>1</sup> , 130 <sup>1</sup>
34	50	270, 280, 290, 400
25	75	210, 245, 290, 400
17	100	330, 670, 1200, 1700
Substrate		77, 80, 85, 90, 95

<sup>1</sup> Indentations were mostly on the substrate.

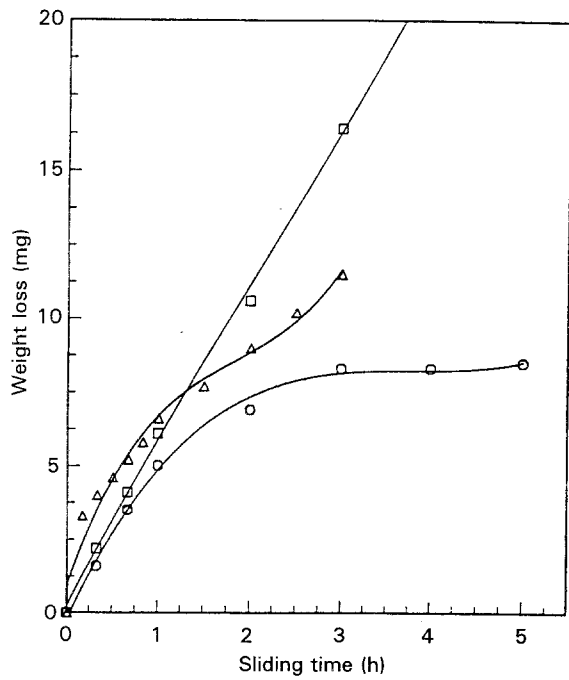


Figure 5 Sliding wear behaviour of: (□) Al-SiC, (○) laser-coated Al-SiC, and (△) 6061-T6 Al.

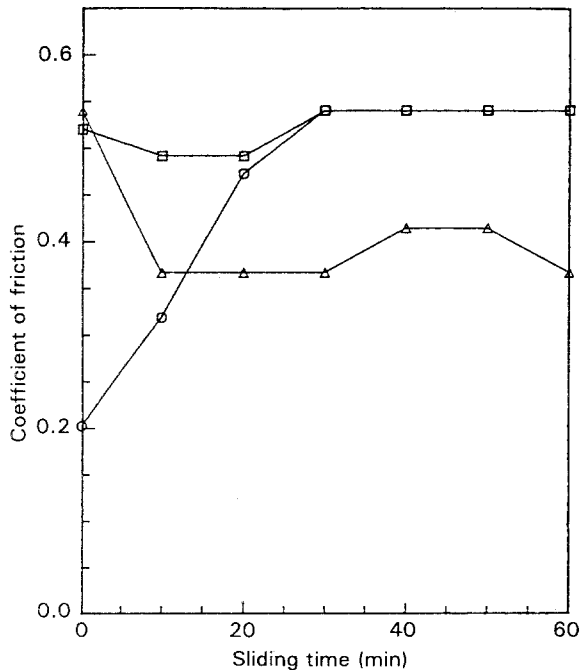


Figure 6 Friction behaviour of: (□) Al-SiC substrate, (○) laser-coated Al-SiC, and (△) 6061-T6 Al.

the same as that of the substrate. To correlate friction and wear, and to identify the friction and wear mechanisms of laser-coated samples, a detailed analysis of worn surfaces is required.

#### 4.5. Corrosion resistance

The anodic polarization curves (Fig. 7) show that the open-circuit potential for the laser-coated and uncoated samples was almost identical. The open-circuit potential for the laser-coated specimen was initially lower and then fluctuated with time. In contrast, the open-circuit potential for the uncoated specimen was

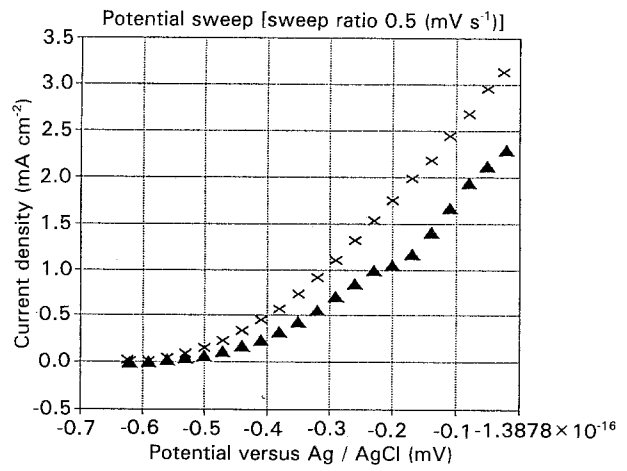


Figure 7 Potentiodynamic polarization curves for (×) Al-SiC substrate, and (▲) laser-coated Al-SiC in 0.1 M NaCl solution.

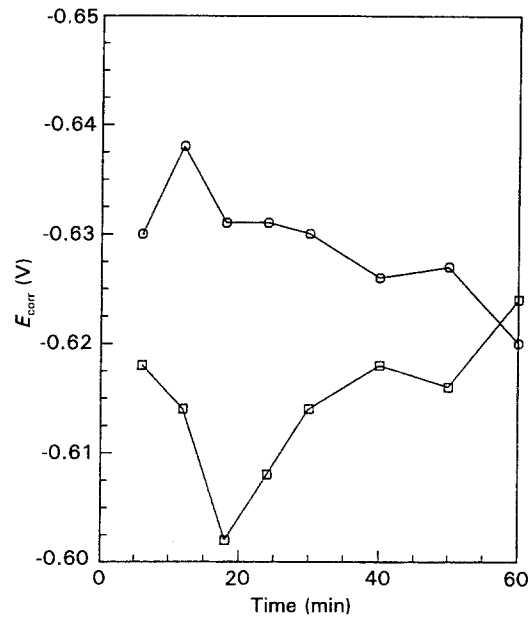


Figure 8 Open-circuit potential as a function of time in 0.1 M NaCl solution for (□) laser-coated Al-SiC, and uncoated (○) Al-SiC specimen.

initially higher and then decreased with time (Fig. 8). After 1 h, the corrosion potential for both specimens was stabilized due to the formation of a passive film.  $E_{corr}$  values for the uncoated and coated samples were  $-0.6260$  and  $-0.6200$  V, respectively. However, the anodic current density for a given potential is lower for the laser-coated Al-SiC implying less susceptibility to pitting corrosion. The plot shows that the laser-coated samples are more passivated with an increase in applied potential.

#### 5. Conclusions

The results of this research indicate that the laser glazing technique, using salt precursors, is a viable and effective method for depositing complex composition coatings on advanced composites. Though X-ray diffraction analysis did not indicate the formation of completely amorphous structures, these experiments, involving laser chemical reduction of metal salts, demonstrate significant evidence for partly crystalline and

partly amorphous structures in the coatings. The formation of these coatings has increased the hardness from 85 to 1700 H<sub>v</sub> depending on the coating thickness, and has improved the wear resistance by almost 50% after 3 h of testing. The anodic current density at a given potential was determined as 2.2 mA cm<sup>-2</sup> for the coated samples, compared with 3.1 mA cm<sup>-2</sup> for uncoated samples; showing a significant improvement in the corrosion resistance of the laser-coated samples.

Further, this process has the ability to form coatings of any complex composition desired. The relative compositions of metallic (e.g. chromium, nickel, cobalt, molybdenum and iron) or non-metallic elements (e.g. boron, carbon and phosphorous) can be varied to enhance the formation of amorphous coatings. Although a comparison with other coating methods, such as chemical vapour deposition, sputtering and electroless plating, has not been made to date, the laser coating process offers several benefits that include the synthesis of amorphous-like microstructures and enhancement in hardness, wear and corrosion resistance of MMCs; indicating that the laser coating process may be technically superior than other methods for providing oxidation, wear and corrosion resistance. The process is versatile and simple. Any combination of elements and compounds can be deposited on the substrate, and there is no need for a vacuum or an inert atmosphere. The process can be carried out at much higher speeds than many other coating processes. The process is adaptable for automation, which in turn will allow coating of large scale structures and complex shaped components.

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