J MATER SCI **41** (2006) 1073–1080

Spray processing and wear characteristics of Al-Cu-Al_2O_3-Pb based composites

M. ANIL, S. N. OJHA
Department of Metallurgical Engineering, Institute of Technology, Banaras Hindu University, Varanasi-221 005, India

The spray deposition process has been employed in synthesis of Al-4.5Cu-10Al_2O_3 and Al-4.5Cu-10Al_2O_3-10Pb based composites. The microstructure and wear characteristics of composites were investigated. The rapid solidification inherent in spray deposition processing resulted in a uniform dispersion of Al_2O_3 and Pb particles co-existing in the matrix of the-primary α-phase. The grain size of the Al-4.5Cu-10Al_2O_3-Pb composite was observed to be higher than that of the Al-4.5Cu-10Al_2O_3 composite in various sections of the spray deposit. The wear rate of composite materials decreased with addition of Pb phase. This behavior is discussed in the light of the microstructural modification induced by spray deposition and the morphology of debris particles on the wear track surfaces. The wear characteristics of the composites are compared with that of the liquid immiscible Al-4.5Cu-10Pb alloy.

1. Introduction

In recent years, continuous attempts have been made in area of alloy design and use of novel processing techniques to synthesize high performance materials. In this direction composite materials have become an attractive alternative to the traditional non-reinforced monolithic alloys. A large number of composite materials have metallic matrices reinforced with high strength, high modulus and often brittle ceramic phase particles. There are various techniques available for processing of particulate reinforced composites. Their salient features have been discussed and reviewed in a number of publications [1, 2]. An understanding of the factors that influence the strength and nature of wear is important for composites, as these properties are sensitive to the type of reinforcements [3] and method of processing [4]. Several investigations have demonstrated improved wear resistance of aluminium alloys reinforced with both hard ceramic phase [5, 6] and soft metals as a second phase [7, 8]. In these studies, the potential of composite materials based on light weight aluminium matrix and ceramic particles, such as silicon carbide, alumina and boron nitrides as dispersed phase, has been greatly emphasized. The wear resistance of Al- Al_2O_3 composites was reported to be superior to those containing SiC [9]. The inferior performance of the SiC reinforced composites is generally attributed to the reaction interface between the Al matrix and SiC. The size and distribution of the second phase particles play an impotent role in controlling the mechanical properties and wear characteristics of materials. A composite with large size Al_2O_3 particle was reported to exhibit properties superior to that containing small size particles [9, 10]. Nevertheless, in all cases the wear rate of composites was at least one order of magnitude lower than that of the non-reinforced alloy matrix. The dispersion of second phase particles and characteristics of the particle/matrix interface significantly depends on the processing methodology of the composite materials.

Early attempts by liquid metallurgy methods to incorporate ceramic particles into the metallic melt had limited success. Most liquid metals do not wet ceramic particles and this results in rejection of the particles from the melt [11, 12]. The importance of the spray forming technique has been emphasized due to several beneficial effects on processing of composites materials by this method. In this processing methodology, high energy gas jets interact with the stream of molten metals and alloys to generate a spray of micron sized droplets which are directed towards a substrate for deposition. The reinforcement phase particles are incorporated in the spray at a suitable distance from the atomizer to mix with the droplets and get simultaneously deposited on the substrate to generate a preform of the composite material [13, 14]. A high rate of heat extraction achievable during solidification of droplets as well as on the deposition surface results in considerable refinement in grain size and chemical homogeneity of the deposits [15–17]. In previous investigations, the effectiveness of Pb particles on improvement in wear resistance

0022-2461 © *2006 Springer Science + Business Media, Inc.*
DOI: 10.1007/s10853-005-3643-7

of spray formed monolithic Al-based alloys was reported [18, 19]. It was shown that the spray formed alloys exhibited a homogeneous distribution of submicron Pb particles in the matrix phase. This effect led to formation of a continuous film of Pb on the mating surfaces at an early stages of wear and protected the matrix phases from further wear. However, the effect of Pb on wear characteristics of spray formed Al-based composite materials has not yet been studied. The present investigation aims at in this direction.

The spray forming of particulate reinforced composite materials based on dispersion of Pb particles in the matrix of Al-4.5Cu alloy and Al-4.5Cu-10 Al_2O_3 composites have been studied. The microstructural and wear characteristics of spray formed composites vis-a-vis that of monolithic alloys are reported.

2. Experimental details

2.1. Process description

The spray deposition system consists of (i) a spray assembly to produce spray of fine droplets (ii) an atomisation chamber wherein spray atomisation takes place in an inert gas atmosphere and (iii) a control system for the gas and metal flow and manipulation of the deposition substrate. A schematic of the spray deposition set-up is shown in Fig. 1. The atomization nozzle constitutes a gas flow channel of convergent-divergent configuration concentric to a straight flow tube. A stream of molten metal, the diameter of which is same as that of internal diameter of the flow tube, then reaches into the atomisation zone. An interaction of high energy gas jets with the melt stream at the tip of the melt delivery tube promotes atomization of the melt into spray of micron size droplets. These are directed towards a substrate to produce a coherent deposit with a considerable refinement in the microstructure and chemical homogeneity of the alloy. The second phase ceramic particles are incorporated in the melt either in the crucible or by directing in the spray to disperse and co-deposit at the substrate.

An Al-4.5% Cu alloy was melted by induction heating in a graphite crucible placed on the top of the atomizer. The Al_2O_3 particles, with a median particle diameter (d_m) of 4.5 μm and standard deviation of particle size distribution (σ) of 1.6, were incorporated in the melt in the crucible. A continuous supply of nitrogen gas was ensured during the melting process to protect the melt from oxidation. The melt was stirred prior to atomisation to ensure complete miscibility of the liquid phase. The atomization of the melt was carried out by Nitrogen gas and the spray was deposited on a copper substrate. This resulted in co-deposition of Al_2O_3 with the spray of droplets of Al-4.5%Cu alloy to give rise to a coherent preform of the composite material. In a similar way, Pb granules were added to the melt in the crucible before atomization to produce spray-deposits of liquid immiscible Al-Cu-Pb alloy. The processing conditions employed during spray deposition are given in Table I.

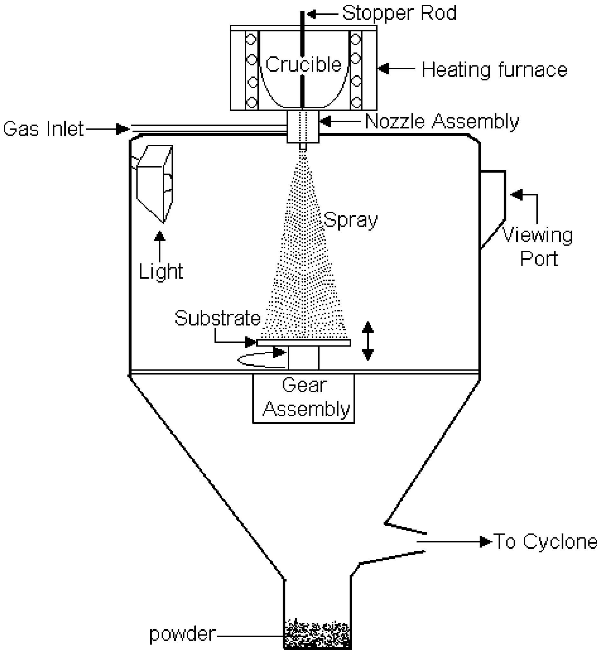


Figure 1 Schematic diagram of the spray deposition process.

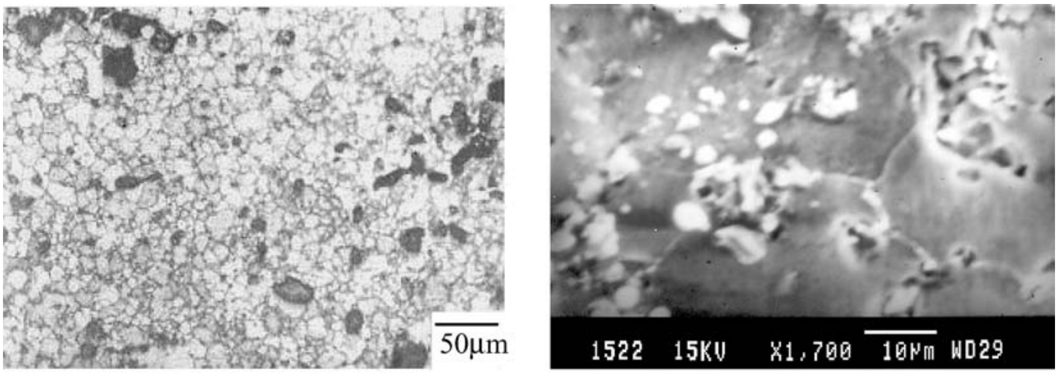
In one of the experiments, two chromel-alumel thermocouples were inserted through a hole in the deposition substrate. These were centered along the axis of the spray. The hot junctions of thermocouples were positioned at a distance of 0.5 mm and 10 mm above the substrate. Thermocouple wires were insulated with silica to avoid their contact with the metal substrate. The spray nozzle and the substrate were leveled to align the thermocouples with the axis of the melt spray. The output of the thermocouples were recorded during and after the spray deposition using a Data Acquisition System with a response time of one second.

2.2. Materials characterization

Several samples from the center and peripheral regions of the spray-deposit were prepared for microstructural examination as well as for the measurement of the porosity of spray deposit. The microstructural investigation

TABLE I Process variables employed during atomization and spray deposition

Alloy composition (wt%)	Melt temperature (K)	Gas pressure (MPa)	Gas/Melt flow ratio	Deposition distance (m)
Al-4.5Cu-10Al_2O_3	1020	0.8	1.05	0.35
Al-4.5 Cu-20 Pb	1100	1.0	1.0	0.30
Al-4.5Cu-10Pb-10 Al_2O_3	1050	1.0	1.1	0.35



(a) (b)

Figure 2 Microstructure of the spray deposited Al-4.5Cu-10Al_2O_3 composite showing (a) Equiaxed grain morphology of the primary α-phase and (b) dispersion of Al_2O_3 particles.

was carried out in a Metallux-3 Optical Metallograph and JEOL 840 A scanning electron microscope. The closed and interconnected porosity were estimated by Xylene impregnation method as described by Arthur [20]. The grain size in various sections of spray-deposit was measured using a VIDS image analyzer.

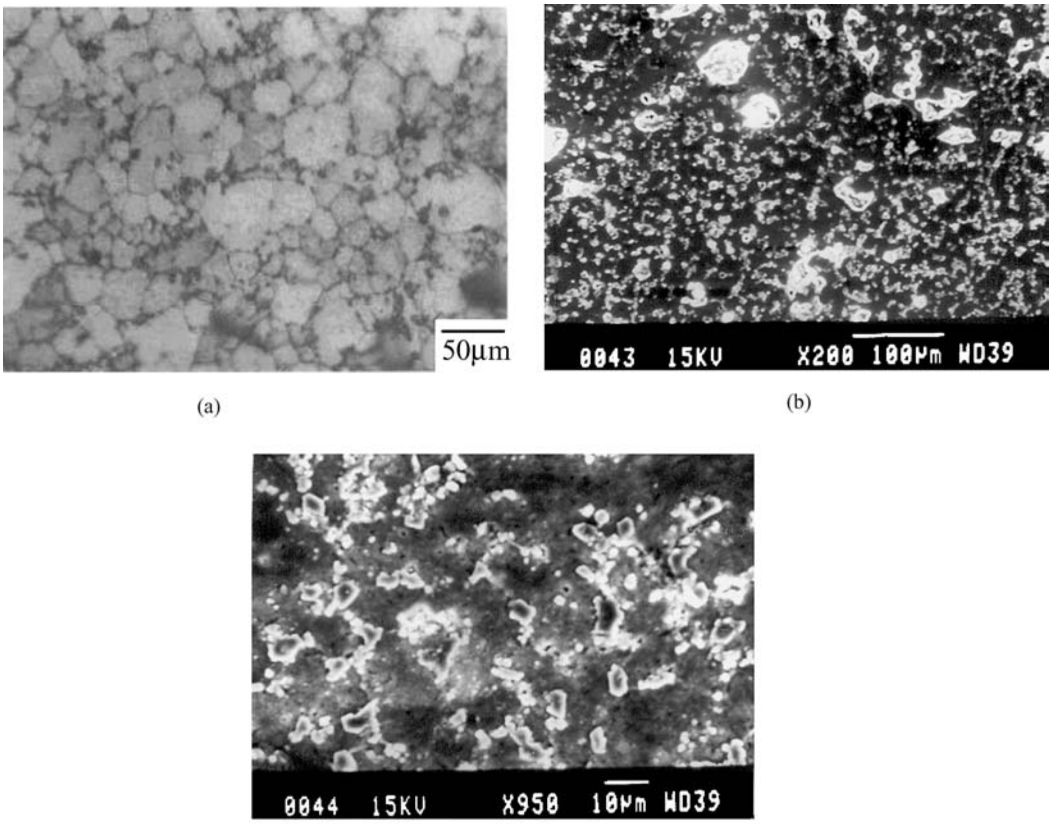
The wear test was carried out on a pin-on-disc type machine. Primarily the experimental set-up consisted of a hardened steel disc of 120 mm diameter connected to a variable speed d.c. motor through a shaft driven by pulley and belt system. The wear test specimen of 8 mm diameter was mounted in a specimen holder attached to the bottom of load pan facing towards the steel disc. The traversing of the specimen holder on the disc facilitated the selection of wear track diameter in this process. The flat surfaces of both the test pin and steel disc were polished to a surface roughness of about 0.5 μm, thoroughly cleaned and dried before the test. The diameter of the wear track was varied from 50 to 100 mm by controlled movement of the specimen holder. The applied load was varied from 10 to 40 N at a constant sliding velocity of 1.1 ms^{-1}. The wear length of the specimen was recorded in a data acquisition system. In the present experiment, all the tests were carried out only in dry sliding conditions and all the data were recorded at room temperature. The wear track surfaces were examined using a scanning electron microscope.

3. Results and discussion

3.1. Microstructural features

The microstructure of the spray formed Al-4.5Cu-10Al_2O_3 composite exhibited a fine equiaxed grain morphology of the primary α-phase with a uniform distribution of Al_2O_3 particles. The preform close to the substrate surface revealed a mixed-grain microstructure wherein large grains were surrounded by the fine grains. However, as the thickness of the deposit increased, a considerable uniformity in the grain size was achieved throughout the section of the deposit (Fig. 2a) and the grain size varied from 15 to 20 μm. Scanning electron microscopy revealed the clustering of Al_2O_3 particles (Fig. 2b). Several interesting features were observed in the microstructure of the spray formed Al-4.5 Cu-10 Al_2O_3-10 Pb composites. The grain size of the primary α-phase increased in all the sections of the deposit (Fig. 3a). The sub-micron size Pb particles were invariably observed throughout the sections of the deposit (Fig. 3b). In some regions, it was difficult to reveal the grain boundaries of the matrix phase due to a large volume fraction of isolated fine Pb particles. The Pb particles were observed to be either isolated or co-existing with Al_2O_3 particles. The sub-micron size particles of Pb were observed to be aligned in a row compared to a random distribution of the larger particles. The microstructure of the liquid immiscible Al-4.5Cu-10Pb alloy indicated both the globular particle of Pb and also a continuous film along the grain boundary (Fig. 4). In addition, several particles exhibited evidence of necking and fragmentation of the Pb-rich phase in the microstructure of the spray-deposit of this alloy.

The presence of an equiaxed grain morphology of the primary phase is consistent with the results of other investigators [14, 16]. However, a relatively low grain size of matrix phase of composites in the present work is a noteworthy feature. The spray deposition processing of composites is influenced by the nature of droplets and their interaction with the reinforcement particles. The atomization of the melt is promoted by its interaction with high velocity gas jets resulting in a wide size range of micron sized droplets. The size and distribution of droplets are governed by process parameters such as melt flow rate, gas flow rate and melt temperature. The cooling rate of the droplets depends upon their size and relative velocity with the gas stream and these have been estimated to fall well within rapid solidification regime [21]. As a result, the spray on the deposition surface comprises of solid particles, semi-liquid and liquid droplets. The spray aggregate on coalescence generates a mushy zone layer on the deposition surface. The fluid flow condition and related rate of heat extraction from the mushy zone controls the grain size and size distribution of the deposit. The fine grain size



(a)

(b)

(c)

Figure 3 Microstructure of the spray deposited Al-4.5Cu-10Al_2O_3-10 Pb composite showing (a) large size equiaxed grains, (b) coexisting Al_2O_3 and Pb particles and (c) clustering of second phase particles.

of the primary α-phase is attributed to the low deposition temperature of the spray. This effect arises as a result of large volume fraction of relatively small size droplets generated in close couple gas atomization process used in the present investigation. The temperature of the spray and its heat content are the crucial parameters which are controlled for the synthesis of the composite materials. This is due to the fact that particle incorporation in the matrix and their uniform distribution depend on these parameters to a large extent. However, during spray deposition of liquid immicible Al-4.5Cu-10Pb alloy, the separation of Al and Pb-rich liquid occurs even during solidification of droplets in flight. The bimodal size distribution of Pb particles in the microstructure of atomized powder particles of this alloy indicates the phase separation process during freezing of the melt. Subsequent to impact on deposition surface, the Pb-rich phase is disintegrated to fine debris due to a turbulent fluid flow condition and resultant shearing action generated on the deposition surface. The debris particles tend to become round during their coarsening stage and generate a uniform distribution of Pb particles in the matrix phase.

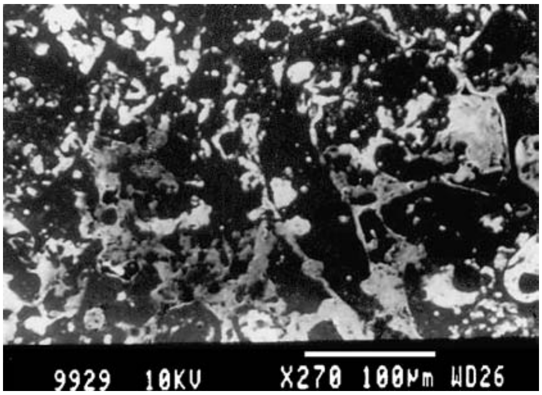


Figure 4 Microstructure of Al-4.5Cu-10 Pb alloy showing globular and elongated shape of Pb particles.

3.2. Porosity and grain size

The spray-deposit of Al-4.5Cu-10Al_2O_3 composites indicated considerable variation in porosity at different sections of the deposit (Table II). A maximum 20% of total porosity was observed towards the top section of the deposit compared to a less than 12% in the central regions of the deposit. However, the maximum amount of porosity in all sections of the deposit was closed porosity. The interconnected porosity was invariably less than 1% against 15 to 20% of closed porosity.

The matrix phase of both the composite materials containing Al_2O_3 and Pb particles showed variation in their grain size in the bottom and peripheral regions of the

TABLE II Variation in porosity at different sections of the deposit of Al-4.5Cu-10Al_2O_3 composite

Location	Total (%) P(T)	Inter-connected (%) P(I)	Closed (%) P(C)	P(I)/P(T)	P(C)/P(T)
Bottom	15.2	0.05	15.15	0.33	99.67
Center	11.8	0.22	11.58	1.86	98.13
Top	20.4	0.60	19.80	2.98	97.06

spray-deposit (Fig. 5). However, the average grain size of the deposit in the central region was observed to increase with increase in deposition thickness. Subsequent increase in the thickness of the deposit the grain size was observed to be considerably uniform. However, the alloy containing Pb phase invariably showed large grain size of the matrix phase in all sections of the deposit for a similar processing conditions.The average grain size of Al-4.5Cu-10Al_2O_3 was estimated to be 18 μm compared to an average grain size of 32 μm of the composites containing 10 wt% Pb.

It is well known that there exists a certain variation in the grain size and the amount of porosity in the spray deposited metal-matrix composites. Except for the common reasons for the formation of porosity in spray deposited preform, addition of reinforcements during spray atomization and deposition further aids to the formation of porosity. This condition arises due to an increase in the viscosity of the melt that causes insufficient flow of the melt into the interstices of particles and facilitates formation of micro-porosity. In addition, the difference in coefficient of thermal expansion between the ceramic phase and the metallic matrix causes contraction misfit between the components during solidification of the melt. This effect has been reported to generate interfacial micro-porosity [22]. The larger the reinforcement particulate, the more such micro-porosity are generated. The presence of porosity lowers the bonding of interface between the reinforcement and matrix phase. Finally, the residual gas on the rough surface of the reinforcement particles enters into the inner part of the droplets with the particles.

The variation in porosity and grain size of the matrix phase at different locations of the deposit is attributed to the nature of solidification condition of droplets as well as the melt on the deposition surface. Although atomized droplets are subjected to cooling rate well within rapid solidification regime, the cooling rate of the spray-deposit is slow as shown by the thermal profile of the spray-deposit. As the spray of droplets strikes the cold substrate with high velocity, a high rate of heat extraction occurs by the mode of conduction. With increase in thickness of the deposit, the heat extraction slows down due to the thermal barrier created by the deposit. Subsequent growth of the deposit occurs under steady-state heat flow condition. This stage of the deposition process results in a uniform grain size of the spray-deposit as shown in Fig. 5. The refinement in grain size of composites containing Al_2O_3 particles may be rationalized on the basis of thermal and nucleation effect on the deposition surface. The incorporation of Al_2O_3 particles in the spray lowers the effective spray enthalpy. In addition, large nucleation sites are also provided by the second phase ceramic particles during solidification of the remaining melt. The grains growing from different nucleation sites converge at common boundaries due to geometrical constraint giving rise to fine grain microstructure of the composites. The grain coarsening is limited during subsequent cooling of the spray-deposit in solid state due to pinning effect provided by second phase particles. These effects together with a lower deposition temperature of the spray in the present investigation result in lower grain size of composite material. However, the Pb content of the other alloy composite increases the spray enthalpy of the deposit and the solidification time of the melt. Consequently, the grain size increases due to coarsening of the primary phase in this alloy composite.

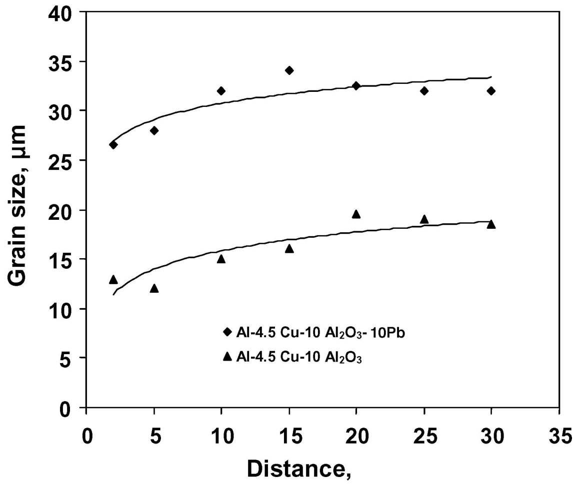


Figure 5 A comparison in grain size of Al-4.5Cu-10Al_2O_3 and Al-4.5Cu-10Al_2O_3-10 Pb composites along the through thickness direction of the deposit.

3.3. Thermal profile of the deposit

The variation in temperature of spray deposit during and after deposition is shown in Fig. 6. These were generated during spray deposition of Al- 4.5Cu-10Al_2O_3 composite produced at a deposition distance of 0.35 m. The thermocouple marked as TC-1 in the above figure was protruded to 0.5 mm above the substrate surface whereas that marked TC-2 recorded the temperature at 10 mm above the substrate. The temperature of the deposit 0.5 mm above the deposit—substrate interface was observed to rise rapidly after the start of the spray deposition to a maximum temperature of 578°C and then becomes constant during deposition process. The second thermocouple (TC-2) at 10 mm above the substrate recorded a highest peak temperature of 415°C which further decreased towards the end of the deposition cycle. After the spray deposition both the thermocouples exhibited an exponential decrease in temperature.

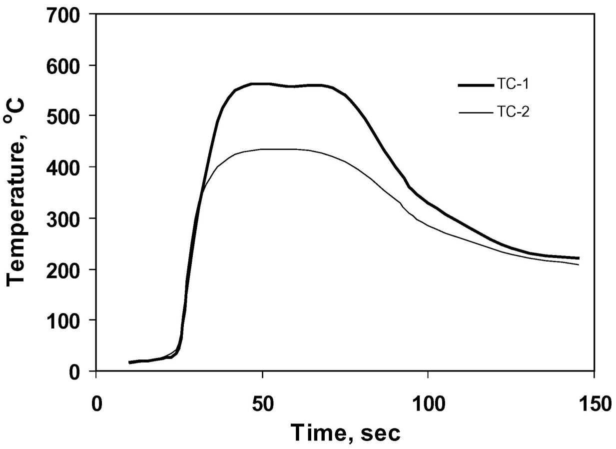


Figure 6 Thermal profile of the spray-deposit at two different locations above the top surface of the substrate.

The results indicate that the two thermocouples yield similar temperature profiles. The thermocouple junction positioned 0.5 mm above the substrate surface measures the temperature history of the spray deposit at early stages of deposition. During spray deposition this temperature sharply increases and during post-deposition cooling the temperature decreases exponentially with time. Both the protruding thermocouples initially measures the temperature of droplets which land on the hot junction. These droplets do not experience cooling by the substrate so their temperature increase before they are embedded in the spray-deposit. The first thermocouple reaches this condition at an early stage. When the thickness of the deposit increases, there is a variation in temperature at two locations of the thermocouples during spray deposition. Whereas the post-deposition temperature profile exhibits large temperature gradient across the deposit thickness.

3.4. Wear characteristics

The wear rate of the spray formed composite materials varied as a function of applied load (Fig. 7). The wear rate continuously increased with applied load in Al-4.5Cu-10Al_2O_3 composite. This wear behavior of the composite was observed to be similar to that of Al-4.5Cu-10Pb alloy. However, the composite materials showed a low rate of wear at a lower applied load which increased rapidly at load exceeding 25 N. In contrast, the alloy containing 10% Pb initially indicated a higher wear rate compared to the composite materials which decreased continuously beyond an applied load of 25 N. The alloy containing both the Pb and Al_2O_3 particles invariably indicated a relatively low wear rate compared to that of composite and the liquid immiscible alloy with two distinct regions of wear. The first regime of mild wear was observed upto an applied load of 30 N. The second regime pertained to severe wear at the load exceeding 30 N. The examination of the wear track surfaces indicated adhesive and abrasive wear of metallic materials (Fig. 8). Scoring and fine debris particles were characteristically observed on the wear surface of composites containing alumina particles (Fig. 8a). This characteristic was observed in the test pin subjected to a higher load during the wear test. On the other hand, the composite containing Pb phase exhibited smearing of Pb particles on the wear track surface that developed a continuous film (Fig. 8b). This feature was observed in the sample tested even under higher applied load conditions. Similarly, smearing of Pb phase was also observed in the sample of Al-4.5Cu-10Pb alloy under a low applied load (Fig. 8c). However, as the applied load was increased, the continuity of the Pb film ceased.

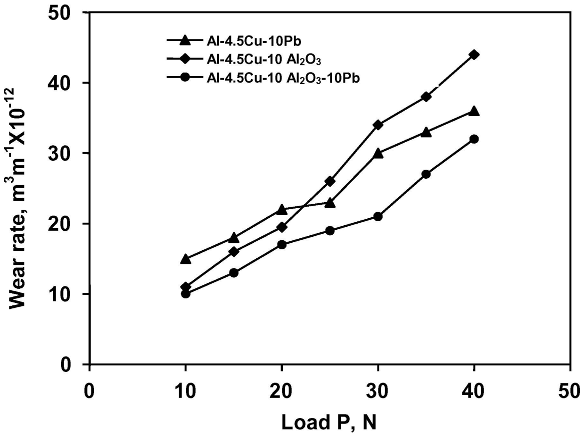
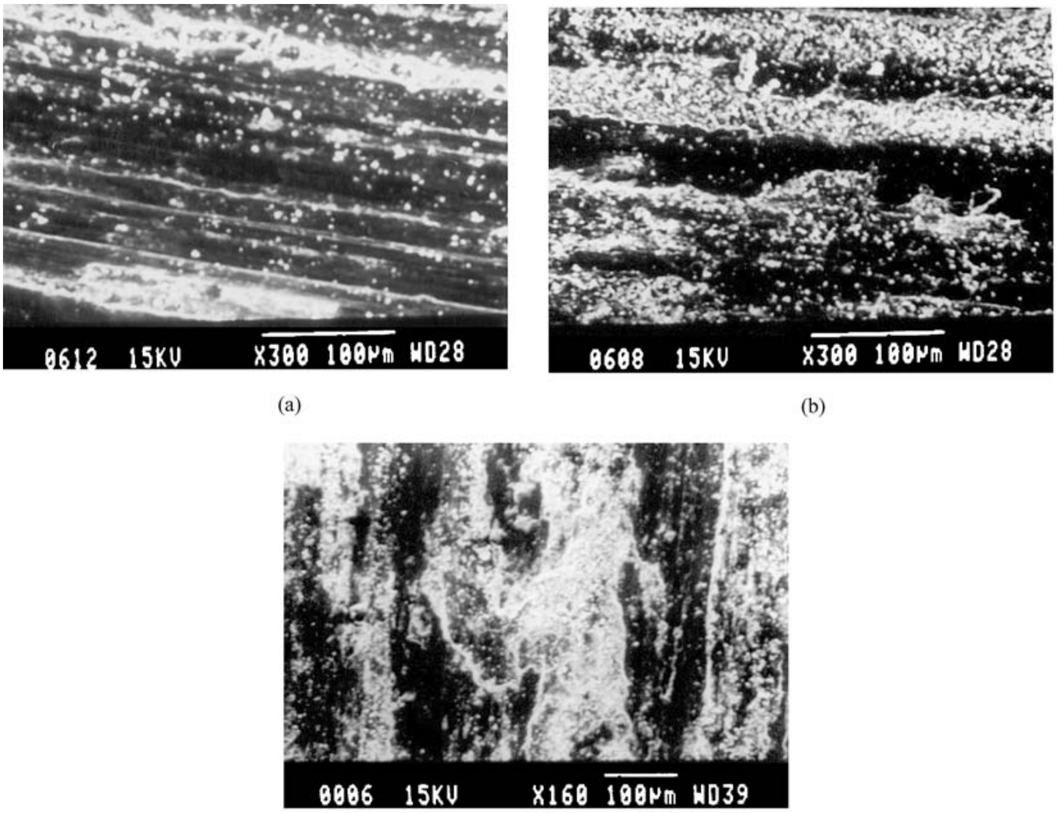


Figure 7 Variation in wear rate of composites and liquid immiscible alloy as a function of the applied load.

Earlier investigators [23, 24] have reported similar results on wear behavior of a large number of metals and alloys and their composites produced by different processing techniques. It has been explained that Pb particles act as a solid lubricant between the mating surfaces by smearing over the substrate and forms a continuous film. The initial decrease of wear rate under low load may be visualized due to rise in temperature of the mating surfaces which promotes formation of protective films of lead thereby lowering the wear rate. However, when the applied load exceeds a critical value, the Pb film becomes discontinuous and consequent increase in the wear rate takes place. The stability of the lubricating film continues up to a higher applied load in the Al-4.5Cu-10Al_2O_3-10Pb alloy composite. Consequently the specimens show consistently a lower wear rate compared to the composite materials without Pb phase. At the early stages of testing, the composite materials show a lower wear rate than the monolithic liquid immiscible alloy. This effect is attributed to the oxidative nature of the wear condition as indicated by the co-existing fine and coarse mixture of lead and oxide particles on the wear track surfaces. On the other hand, the hard and strong matrix of Al-4.5Cu -Al_2O_3 composite material, is forced deeper by the asperities present on the surfaces. This causes extrusion and smearing of lead over the test pin surface.

In summary, the results of the present investigation indicate that an effective microstructural control with a homogeneous dispersion of coexisting small size Al_2O_3 particles and submicron size Pb particles in the Al-matrix



(a) (b) (c)

Figure 8 Microstructure of the wear track surfaces of composites showing (a) scoring in test pin of Al-4.5Cu-10Al_2O_3 composite, (b) smearing of Pb particles in Al-4.5Cu-10Al_2O_3-10 Pb composite and (c) continuity of Pb film on wear surface of Al-4.5Cu-10 Pb alloy.

is achieved during spray deposition processing. These microstructural features lead to improvement in wear characteristics of composites as well as that of the monolithic liquid immiscible alloy.

4. Conclusions

1. The microstructures of the composite materials produced by the spray forming process show an equiaxed morphology of the matrix phase with a uniform distribution of second phase Al_2O_3 particles. The spray-deposits of the liquid immiscible alloys exhibit ultrafine particles of Pb in the matrix of the primary α-phase.

2. The grain size varies along the thickness of the spray deposits. A mixed grain microstructure observed near the bottom section of the deposit changes to a uniform grain microstructure with increasing thickness of the deposit. The grain size of the Al-4.5Cu-10 Al_2O_3 composite was invariably lower than the composite materials containing Pb-rich phase. The porosity varies from 12 to 20% in different locations of the deposit, the maximum being in the top regions of the deposit.

3. Two different locations of the spray-deposit indicate a similar temperature profile. The temperature initially rises rapidly and reaches to a maximum temperature followed by their exponential decrease towards the end of the deposition cycle.

4. A homogeneous distribution of Pb particles in the matrix phase of the spray formed Al-Al_2O_3 composites exhibits their improved wear resistance compared to that of the composite materials produced without addition of Pb phase. This effect is observed to be more pronounced at higher applied load during the wear test.

References

1. D. J. LLOYD, *Inter. Mat. Rev.* **39** (1994) 1.
2. T. S. SRIVATSAN, T. S. SUNDARSHAN and E. J. LAVERNIA, *Prog. Mat. Sci.* **39** (1995) 317.
3. T. T. LONG, T. AISAKA, M. OSE and M. MORITA, *J. Jpn. Inst. Met.* **51** (1987) 864.
4. T. T. LONG, T. NISHIMURA, T. AISAKA, M. OSE and M. MORITA, *Trans. Japan Inst. Met.* **29** (1988) 920.
5. M. K. SURAPPA and P. K. ROHATGI, *J. Mater. Sci.* **16** (1981) 983.
6. B. C. PAI, S. RAY, K. V. PRABHAKAR and P. K. ROHATGI, *J. Mater. Sci. Eng.* **24** (1976) 31.
7. J. P. PATHAK, S. N. TIWARI and S. L. MALHOTRA, *Wear* **112** (1986) 341.
8. P. R. GIBSON, A. J. CLEGG and A. A. DAS, *ibid.* **95** (1984) 193.
9. K. J. BHANSALI and R. MEHRABAIN, *J. Met.* **9** (1982) 30.
10. K. SOMA RAJU, V. V. BHANU PRASAD, G. B. RUDRAKSHI and S. N. OJHA, *Powder Met.* **46** (2003) 219.
11. F. A. BADIA and P. K. ROHATGI, *Trans. AFS* **77** (1969) 402.
12. A. M. PATTON, *J. Inst. Met.* **100** (1972) 197.
13. S. N. SINGH and S. N. OJHA, *Metals Materials and Processes* **3(1)** (1991) 29.

14. M. GUPTA, J. J. EISLAS, W. E. FRAZIER, F. A. MOHAMMED and E. J. LAVERNIA, *Met. Trans* **23B** (1992) 719.
15. A. K. SRIVASTAVA, S. N. OJHA and S. RANGANATHAN, *Met Mater. Trans.* **B 29** (1998) 2205.
16. Y. WU, J. ZHANG and E. J. LAVERNIA, *ibid.*, **25** (1994) 135.
17. V. C. SRIVASTAVA, A. UPADHYAYA and S. N. OJHA, *Bull. Mat. Sci.* **23 No2** (2000) 73.
18. S. N. OJHA, O. P. PANDEY, B. TRIPATHI and C. RAMACHANDRA, *Mater.Trans. JIM* **33** (1992) 519.
19. G. B. RUDRAKSHI, V. C. SRIVASTAVA, J. P. PATHAK and S. N. OJHA, *Mat. Sci & Engg.* **A383** (2004) 30.
20. G. ARTHUR, *J. Inst. Metals* **83** (1954) 1329.
21. P. SHUKLA, R. K. MANDAL and S. N. OJHA, *Trans.Indian Inst. Met.* **57** (2004) 283.
22. E. J. LAVERNIA, J. D. AYERS and T. S. SRIVATSAN, *Int. Mat. Rev.* **37** (1992) 1.
23. S. MOHAN, V. AGRAWALA and S. RAY, *Z. Metallkunde* **80** (1989) 439.
24. J. P. PATHAK and S. N. OJHA, *Bull. Mater. Sci.* **18** (1995) 975.

Received 1 March 2004
and accepted 25 May 2005