International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.5, No.5, pp 2165-2172, July-Sept 2013

Enhancing The Interphase Strength Of Aluminium Composite By Autocatalytic Process

V.Umasankar[1], S.Karthikeyan[2]* , M.Anthony Xavior[1],

[1]School of Mechanical and Building Sciences, VIT University, Vellore-632014,India.
[2]Surface Engineering Research lab, Centre for Nanobiotechnology, VIT University, Vellore, India.

***Corres. Author: skarthikeyanphd@yahoo.co.in**

Abstract: An attempt has been made to improve interphase strength of reinforcement and matrix by autocatalytic deposition route. The auto catalytic copper has improved the interphase strength which has been validated by radial crushing test as per ASTM 939-09. The ultimate failure load and the compressive strength of the composite has enhanced to an extent of 66.74% in comparison with uncoated reinforcement. The existence of copper on SiC reinforcement has been explained by SEM-EDAX analysis.
Keywords: Matrix, Composites, Coating, Interfacial.

Introduction

Metal matrix composites (MMC) represent an alternative to conventional materials for the production of high performance materials. The materials can be manufactured in such a way as to exhibit a combination of the characteristics of the metallic matrix and the reinforcement phase. The characteristic profile thus developed can be adapted to the respective requirements of application and an optimal utilization of the characteristics of matrix and reinforcement component is made possible. Matrix and reinforcement components have shared interphase, which are absolutely necessary for the fulfillment of the tasks undertaken by the MMCs. Compared with monolithic materials the microstructure and the interphases of metal matrix composite materials cannot be considered in isolation, they are mutually related. Chemical interactions and reactions between the matrix and the reinforcement component determine the interphase adhesion, modify the characteristics of the composite components and affect the mechanical characteristics significantly. The formation of the interphase between the matrix and the reinforcing phase has a substantial influence on the production and characteristics of the metallic composite materials. The adhesion between both phases is usually determined by the interaction between them.[1] .

Aluminium alloy composite with SiC though results in better strength ,thermal expansion and wear resistance has problems in achieving suitable and effective bonding between SiC and aluminium alloy particles and controlled porosity. The possible solution lies in plating of SiC particles with copper .According to Su and Chen [2] , copper coated SiC reinforcement with Aluminium alloy matrix was proved to improve interfacial bonding and improved mechanical properties along with improvement in fracture characteristics.Pay yih et al .,[3] have also reported improvement in mechanical properties of copper SiC reinforced Aluminium alloy matrix. As the reinforcement fraction increases inter particle distance between SiC particles reduces and Sic to SiC contact and bonding becomes a reality .But on account of lower sintering tempering temperatures employed in aluminium composites ineffective bonding take place between reinforcement particles and which is major factor in influencing the fracture characteristics. This was observed in the current study of the uncoated SiC reinforced composite under radial compression.

The chemical and physical characteristics of the reinforcement and the matrix particles plays a vital role in the resulting behavior of the composite due to the effect of the interphase strength as the processing conditions influence the end strength of the composite[2].Metal matrix composites manufactured by powder metallurgy are restricted by low reinforcement percentage due to direct reinforcement to reinforcement contact happening with higher volume fraction of reinforcement. The direct reinforcement particle contact decreases the quality of sintering at the processing temperature because the ceramic reinforcement has higher melting temperature than the sintering temperature which is lower than the temperature of melting of the reinforcement. The ineffectively sintered ceramic particles constitute defects in the composite. Further excessive reinforcement particles contacts leads to high composite porosity since these contacts hinder solid state flow of the softened matrix through the ceramic particles to fill the interstices.[3] The mechanical behaviour of the interphases formed after reactions between coatings and composite constituents is critical, and strongly influences the macroscopic mechanical properties of the composite. Therefore, properties of the reaction interphases formed must be known. A suitable engineered interphase can significantly optimize the strength and the toughness of the composite, and improve its processability and environmental behavior. [4]. SiC particles increases the porosity of sintered composites proportional to the volume percentage and prevents effective self diffusion of copper or Al particles while sintering.These problems can be circumvented by coating the ceramic particles with metallic coating like Copper. Copper is a pink coloured, soft and conducting materials widely used in electronic gadgets , weapons , conducting wires [5-9]. It offers better bondability and solderability. It is invariably added as an alloying element with aluminium with potential for precipitation hardening through additive process. The copper reduction can be carried out with aid of formaldehyde as reducing agent. It has also been reported that coating of the particles activates sintering process by means of interdiffusion and structure of the coating. Coating helps in achieving better compressibility, better homogeneity and distribution along with increased interphase. [Fleming]Al-Cu system undergoes liquid phase sintering and enhances better inter particle diffusion and effective filling of voids by capillary force and improves sinterability.

$Cu^{2+} + 2HCHO + 4OH^{-} \rightarrow Cu + 2HCOO^{-} + 2H_2O + H_2$. For deposition to take place, the negative reduction potential of the reducer should be higher than that for the metal which is to be deposited. The oxidation-reduction potential for the oxidation reaction becomes less positive when the acidity of the autocatalytic solution is enhanced. However, autocatalytic copper deposition process with formaldehyde as the reducing agent requires alkaline medium .Apart from formaldehyde other reducing agents such as hypophosphite[l0-11], borohydride [12 -13] hydrazine[14], dimethylamine borane [15], glyoxylic acid[16] and redox-pairs [17] (i.e. Fe(II)/Fe(III), Ti(III)/Ti(IIII), Cr(II)/Cr(III), V(II)/V(III)) were reported as reducers in autocatalytic copper plating process**.** It is expected that the presence of copper on the surface of the silicon carbide reinforcements will enhance sintering by the formation and flow of Al-Cu liquid eutectic into porous areas, and provide a strong, ductile bond between the reinforcement and the matrix. Hence, the objective of this paper is to compare the performance of MMC's reinforced with autocatalytic copper-coated and un-coated silicon carbide so as to enhance the interphase strength. Other work has been carried out on the electroless deposition of metallic coatings on particulate materials and these resulted in improved processing parameters, such as enhanced infiltration and reduced SiC/Al reactivity [18-25].

Experimental procedure:

AA 6061 gas atomized powders from AMPAL was used as matrix material and SiC particles from Carborundum universal was used as reinforcing materials. Chemical composition of the powders of both matrix and the reinforcement is presented in the table 1 and 2. Powders were characterised for size distribution and shape (fig 1a, 1.b & figure 2 and table 3). The Powders were coated with copper by electroless method using the following composition.

Copper Sulphate (CuSO4)	- 0.02 M
Ethylenediaminetetraacetic acid (EDTA)	- 0.1 M
Formaldehyde (CH2O)	- 0.09M
Sodium Hydroxide (NaOH)	- 0.15M
Triethanolamine	- 10 ml/L
Benzylidene acetone (Brightner)	- 0.0068M

N-ethyl perfluoro-octane-sulfonamide (Surfactant) - 0.0012M

The operating temperature was maintained at 60°C. The powders were subjected to sensitization in stannous chloride solution for 2 minutes followed by activation by palladium chloride solution of composition as described earlier [28]. The required quantity of SiC particles were mixed with known volume of surfactant to avoid agglomeration and made as a paste.

It was washed with distilled water and introduced into auto catalytic plating bath with constant of agitation of 200 rpm. The autocatalytic deposition of copper on SiC was visualized by strong evolution of hydrogen gas. The deposition time was 30 minutes. After plating, the powders were removed from plating bath, washed with distilled water and then dried in sunlight. Then the dried powders were crushed and then compacted.

After that it was ensured no agglomeration appeared in the powders. The coated and uncoated powders were mixed uniformly and compacted in a universal testing machine of 60 T capacity. Compacting is carried out with 350 MPa, 450 Mpa and 550 MPa. Compacted specimens are sintered in nitrogen atmosphere with sintering temperatures of 400,500 and 600 deg C and sintering time varied from 1 to 3 hours. The required quantity of SiC particles were mixed with known volume of surfactant to avoid agglomeration and made as a paste. Then the paste was washed with distilled water and introduced into auto catalytic plating bath with constant of agitation of 200 rpm. The autocatalytic deposition of copper on SiC was visualized by strong evolution of hydrogen gas. The deposition time was 30 minutes. After plating, the powders were removed from plating bath, washed with distilled water and then dried in sunlight. Then the dried powders were crushed and then compacted.

After that it was ensured no agglomeration appeared in the powders. The coated and uncoated powders were mixed uniformly and compacted in a universal testing machine of 60 T capacity. Compacting is carried out with 350 MPa, 450 Mpa and 550 MPa. Compacted specimens are sintered in nitrogen atmosphere with sintering temperatures of 400,500 and 600 deg C and sintering time varied from 1 to 3 hours. Compacts are of 20 mm in diameter and 10 mm in thickness.

These specimens were wire cut to make 20 mm diameter and 10 mm diameter hollow specimens. Radial crushing testing (INSTRON 8801, UK) as per ASTM 939-09 was used to evaluate the strength of the composite which is universally a test carried out by PM industries for accepting the process and powders for production purpose. As the interphase strength increases it is said to increase the radial crushing strength.[Fig 3 a & b]

Table 1. Chemical composition of the powders of reinforcement

Grit	BATCH NO	Particle Diameter m> Volume (%)		
		ds3	ds50	ds94
F 280	Specification	59 Max	35.00-38.00	22.00 Min
	MB 189	51.98	35.17	25.47
Grit	BATCH NO	Particle Diameter <m> Volume (%)		
		ds3	ds50	ds94
F 280	Specification	59 Max	35.00-38.00	22.00 Min
	MB 189	51.98	35.17	25.47

Table 2. Chemical composition of Matrix

Sample ref.	Fe wt %	Si Wt.%	Mg.Wt.%	Cu.Wt.%	Zn.Wt %
AA6061	0.19	0.56	0.94	0.27	0.03

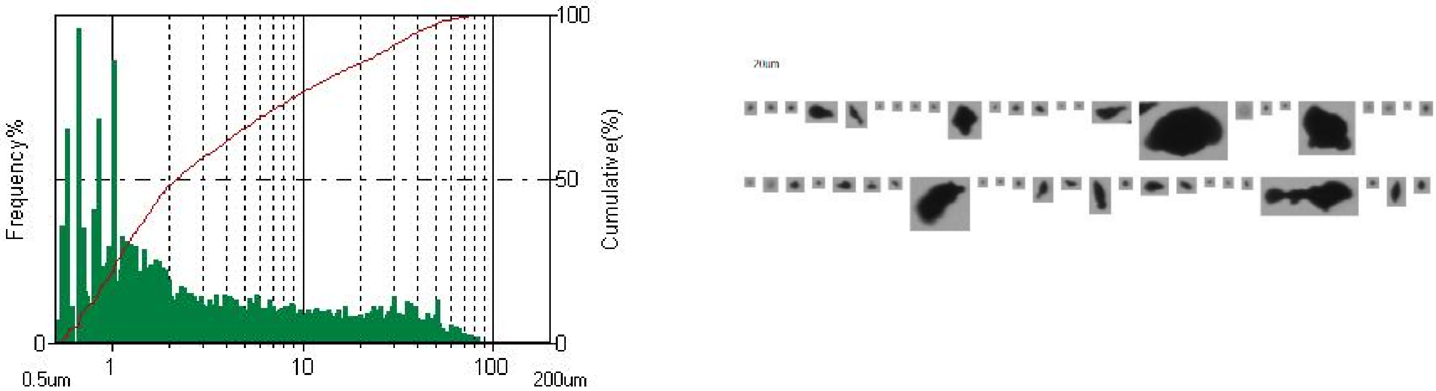

Fig. 1a&b Matrix particles shape analysis

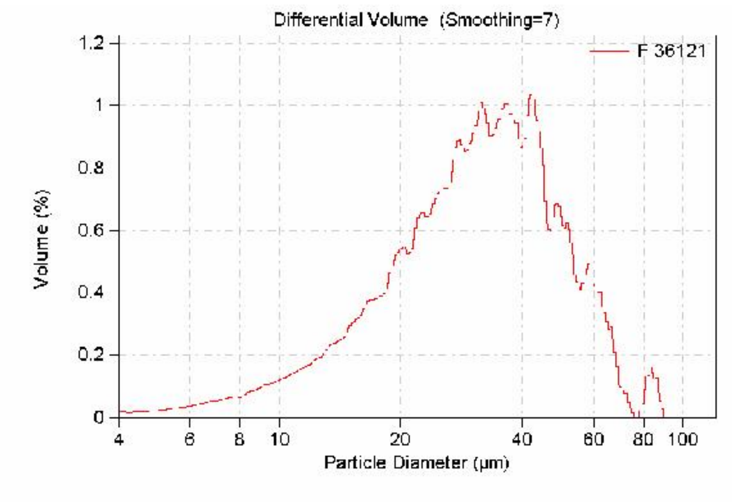

Fig 2. Shape analysis of matrix

Table 3. Size distribution of matrix particles

Particle Circularity Distribution Details									
Over All	0.75-0.9	INDENTING0.	ROLLING	SLIPPING	d50(v)	> d50 Ψ	> 5µm Ψ	> 7µm Ψ	Fines (<5Mic,v)
0.892	37.78	28.24	17.82	53.94	52.61	0.818	0.821	0.816	0.07

Results and discussion

The results of radial crushing carried out for interphase strength analysis is presented in fig 3- 6 and summarized in table 4. From fig 4 and 5 indicate the improvement in the ultimate breaking load with copper deposition of reinforcement particles for 5% SiC. Fig 6&7 give improvement in the above mechanical strength by autocatalytic copper coatings on 15% SiC . Table 4 reveals that the ultimate breaking load and compressive strength have increased by 5.77% for 5% SiC at 600 °C and 66.74% for 15% SiC incorporation at 500°C.

The difference in improvement might be on account of higher sintering temperature resulted in increase of porosity and void nucleation with additional defects. As the eutectic melting temperature of AA 6061is 524°C, which is nearer to the present study at 500°C resulted in enhanced diffusion and inter-particle bonding facilitated by copper. It is line with the concept of activated sintering which is established that doping of the reinforcement increases the densification.

The incorporation of copper particles on SiC which diffuses over the aluminium alloy matrix particles by penetration into the grain boundaries eases intermetallic bonding and thereby improves the strength of composites. The major impediment in productionizing metal matrix composite (MMC) by powder metallurgy route is poor interphased on account of which applications have not progressed in spite of early innovations in the field. The findings of this study will enable development of light weight composite engineering parts for automotive industry like oil pump gerotors. The study also shows that incorporation of autocatalytic copper coatings on SiC not only improves the radial pressing strength but also improves the strain to fail.

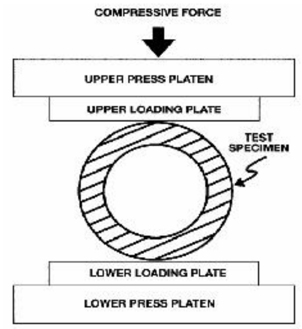

Fig 3 (a) Radial crushing set up

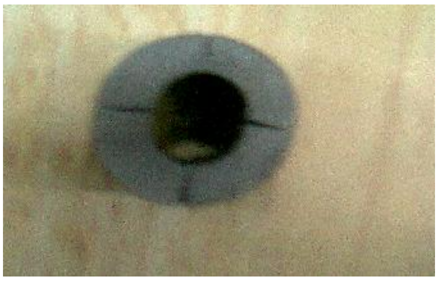

Fig.3(b) Specimen after crushing

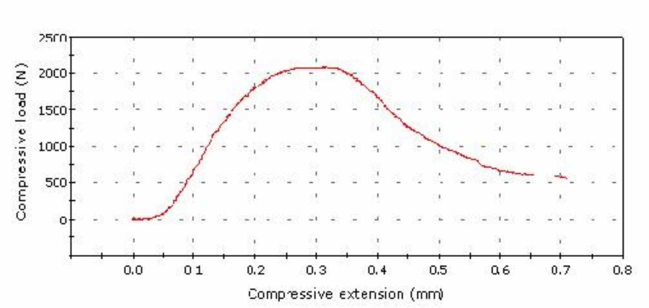

Fig 4. Load Vs deflection curve for 5% uncoated SiC

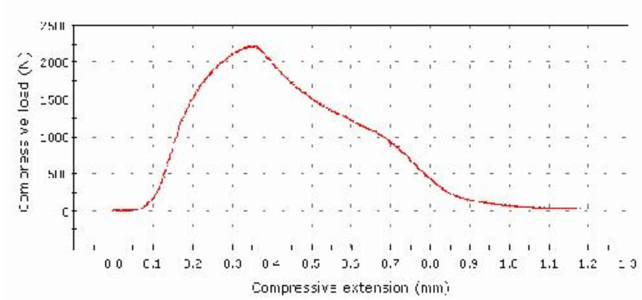

Fig.5. Load Vs deflection curve for 5% coated SiC

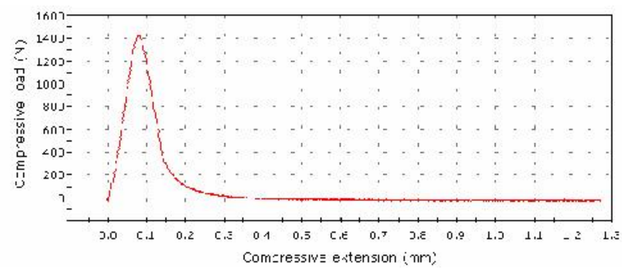

Fig.6. Load Vs deflection plot for 15% uncoated SiC

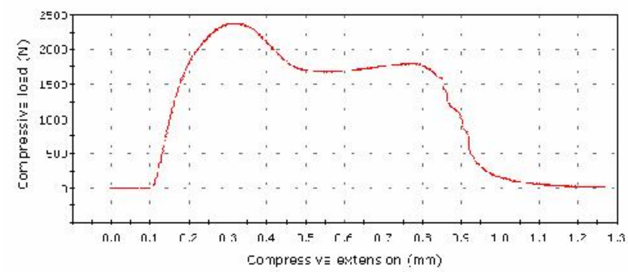

Fig.7.Load Vs deflection plot for 15% coated SiC

Table 4. Radial crushing results carried out for interphase strength analysis

Reinforcement	Coating	Compacting Pressure	Sintering Temperature	Sintering time	Ultimate breaking Load	Compressive strength	Improvement
5%	Nil	550 MPa	600º C	3 Hours	2096.909 N	125.81MPa	
5%	Copper	550 Mpa	600ºc	3 Hours	2217.346 N	133.04 MPa	5.77%
15%	Nil	550 Mpa	500º C	1 Hour	1428.366N	85.70 MPa	
15%	Copper	550 Mpa	500º C	1Hour	2381.938N	142.91 Mpa	66.74%

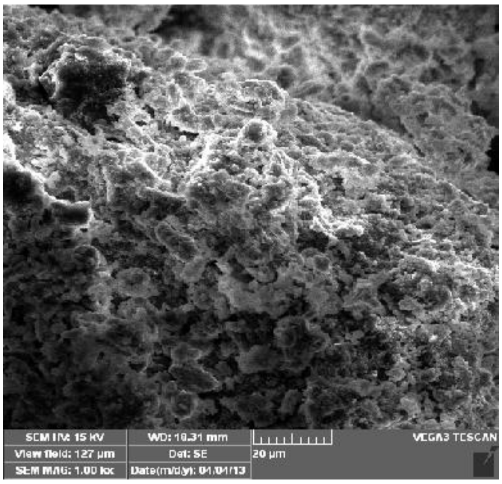

Fig 8.SEM image for fractured specimen X,1000

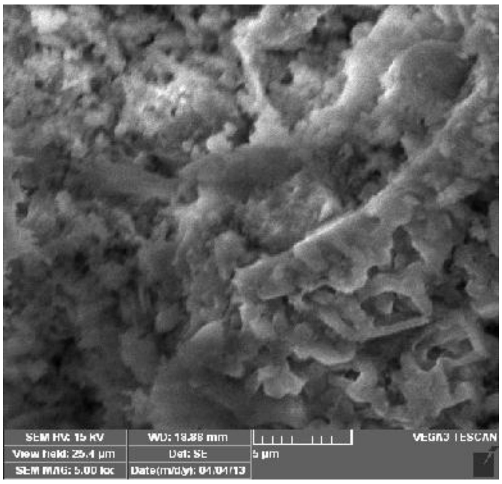

Fig 9.SEM image for fractured specimen X,5000

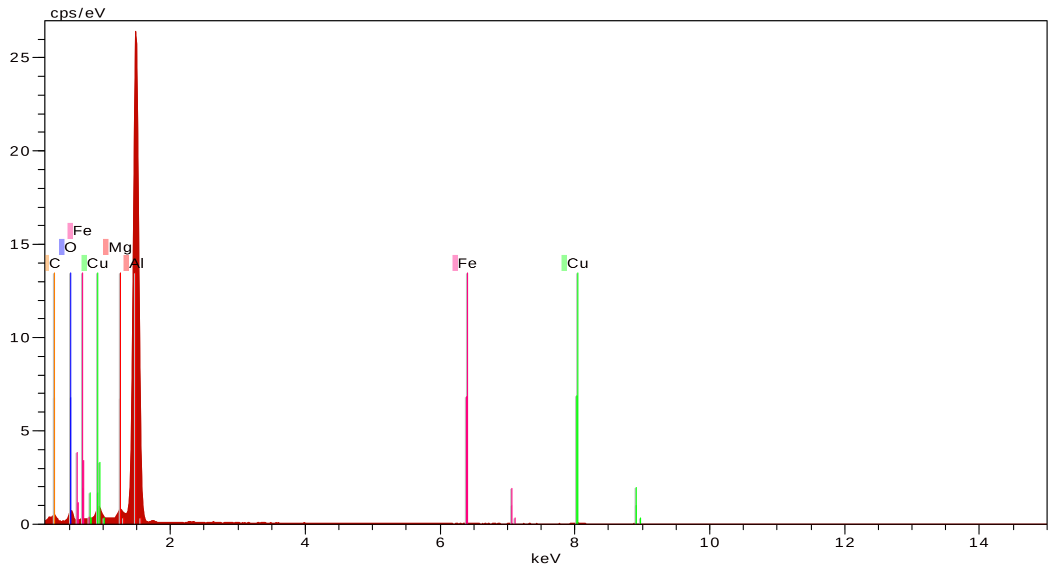

Fig.10.EDAX analysis results of specimen after fracture

Scanning Electron micro graphs studies:

The micro fracture surface shown in Fig. 8 is resembling honey comb structure establishes the ductile failure mechanism which is also evidence from load Vs deflection graph and there was no evidence of fractured particles. It was visualized that the copper-coated silicon carbide reinforced specimens enhanced the bonding between the copper-deposited SiC particles and the aluminium alloy matrix, by way of permeating the applied force to be transferred effectively and uniformly to the reinforcement particles and thus permitting greater strains to cause failure of the composites. The presence of layered copper coated SiC particles portrayed at 5K magnification [Fig.9] indicates the formation high ductility which is in correlation with the results of load vs deflection curve by giving flatter and extended capacity to bear the compressive load before failure. There was again evidence of ductile failure in the matrix and the arrowed part of Fig. 9 highlights a very fine dimple network that probably developed at a particle/matrix interphase. The electron micrograph also exhibited a uniform distribution and absence voids and effective bonding.. Similar observation hass been made for electroless deposition of copper on steel.[26-28]. EDAX showed the presence of copper in two different sharp which is in line with existence of copper both as an alloying element and coated copper on reinforcement. Other peaks like Fe and carbon are impurities embedded during compacting at higher pressures.

Conclusion:

The major conclusions drawn from the study were:

1. A suitable formulation for obtaining uniform deposition of copper by autocatalytic process has been made.
2. The incorporation of copper on SiC resulted in substantial improvement of inter phase strength of MMC.
3. Strain to failure and compressive strength have significantly increased by the co deposition of copper in to SiC particles.
4. The SEM – EDAX analysis established incorporation copper into SiC which invariably reduced the porosity and prevented void nucleation.
5. Ultimate fracture load and compressive strength of coated SiC reinforced specimen has improved by 66% compared with uncoated SiC reinforced specimen.

References:

1. Metal Matrix Composites. Custom-made Materials for Automotive and Aerospace Engineering. Edited by Karl U. Kainer. 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim,ISBN: 3-527-31360-5,p 1-4.
2. X.F.Su,H.R.Chen,D.Kennedy and F.K.Williams ,Effects of interphase strength on the modes and mechanical behaviour of metal-matrix composites,Composites Part A.30,1999,p 257-266.
3. Pay Yih., Chung, D.D.L., 1995. Powder metallurgy fabrication of metal matrix composites using coated fillers, The international journal of powder metallurgy 31, p.335.
4. Campo, M., Uren, A., Rams, J., 2005. Effect of silica coatings on interfacial mechanical properties in aluminium—SiC composites characterized by nano indentation, Scripta Materialia, 52.p. 977.
5. K. Flemmig, K.-P. Wieters, B. Kieback,Sintering Behaviour of coated particles ,Sintering ’05,p 21-24.
6. A.K.Jha,S.V.Prasad,G.S.Upadhyaya ,Controlled Interphases in composite materials,1990,p829-840.
7. R.Ivanus ,Effect of process parameters ,particle characteristics and metallic coating on SiCp copper alloy matrix composites ,Advanced Materials Research,Vol23,2007,p 143-146.
8. Kinga Tomolya,ZoltanGacsi.Arpad Kovs Material Science Forum Vol473-474,2005,p159-164.
9. Lee, H., Wong, S.S., and Lopatin, S.D., J. Appl. Phys., 2003, 93, p. 3796.
10. Brongersma, S.H., Kerr, E., Vervoort, I., Saerens, A., and Maex, K., J Mater Res, 2002, 17, p. 582.
11. Hasegawa, M., Hirai, Y., J. Appl. Phys., 2001, 90, p. 2792.
12. Lingk, C., Gross, M.E., J. Appl. Phys., 1998, 84, p. 5547.
13. Jiang, Q.T., Gross, M.E., Bersuker, G., Foran, B., Mikkola, R., Carpenter, B., and Oemando, J., Mat. Res. Soc. Symp. Proc., 1999, 564, p. 429.
14. Lee, H., Nix, W.D., and Wong, S.S., J. Vac. Sci. Technol. B, 2004, 22, p. 2369.
15. Vas'ko, V.A., Tabakovic, I., Riemer, S.C., and Kief, M.T., Microelectron. Eng., 2004, 75, p. 71.
16. Vas'ko, V.A., Tabakovic, I., and. Riemer, S.C, Electrochem. Solid-State Lett., 2003, 6, p. 100.
17. Moffat, T.P., Bonevich, J.E., Huber, W.H., Stanishevsky, A., Kelly, D.R., Stafford, G.R., and Josell, D., J. Electrochem. Soc., 2000, 147, p. 4524.
18. Lagrange, S., Brongersma, S.H., Judelewicz, M., Saerens, A., ervoort, I., Richard, E., Palmans, R., and Maex, K., Microelectron. Eng., 2000, 50, p. 449.
19. Brongersma, S.H., Richard, E., Vervoort, I., Bender, H., Vandervorst, W., Lagrange, S., Beyer, G., and Maex, K., J. Appl. Phys., 1999, 86, p. 3642.

20. Lee, C.H., Park, C.O., Jpn. J. Appl. Phys. [1] Reg. Pap. Short Notes, 2003, 42, p. 4484.
21. Stangl, M., Acker, J., Dittel, V., Gruner, W., Hoffmann, V., and Wetzig, K., Microelectron. Eng., 2005, 82, p. 189.
22. Ueno, K., Ritzdorf, T., and Grace, S., J. Appl. Phys., 1999, 86, p. 4930.
23. Fischer, H., Electrochim. Acta, 1960, 2, p. 50.
24. Winand, R., VanHam, P., Colin, R., and Milojevic, D., J. Electrochem. Soc., 1997, 144, p. 428.
25. Winand, R., Hydrometallurgy, 1992, 29, p. 567.
26. Thompson, C.V., Annu. Rev. Mat. Sci., 2000, 30, p. 159.
27. Haba, T., Itabashi, T., Akahoshi, H., Sano, A., Kobayashi, K., and Miyazaki, H., Mater. Trans., 2002, 43, p. 1593.
28. Harper, J.M.E., Cabral, C., Andricacos, P.C., Gignac, L., Noyan, I.C., Rodbell, K.P., and Hu, C.K., J. Appl. Phys., 1999, 86, p. 2516.
29. Zakraysek, L., Metal Finish., 1987, 85, p. 29.
30. Karthikeyan, S., Venkatachalam, G., Narayanan, S., and Srinivasan,KN., Journal of Electroplating & Finishing, 2011, 30 (9), p. 12.
31. Karthikeyan, S., Venkatachalam, G., Srinivasan, KN., Vasudevan, T., and Narayanan, S., Journal of Electroplating & Finishing, 2001, 30 (6), p. 18.
32. Karthikeyan, S., Vasudevan, T., rinivasan, K.N. and John, S., Plating and Surface Finishing (USA), 2002, 79, p. 54.

*****