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~~APPENDIX B~~

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EVOLUTION OF MICROSTRUCTURE AND MECHANICAL PROPERTIES IN LASER INDUCED REACTION COATING OF Al_2O_3 ON SiC/Al_2O_3 COMPOSITE

Narendra B. Dahotre, C. Xiao, W. Boss, M.H. McCay and T.D. McCay

Center for Laser Applications
The University of Tennessee Space Institute
Tullahoma, Tennessee 37388

Abstract

The protection of a $SiC_{(P)}/Al_2O_3$ composite at high temperature from deleterious reactions occurring within and with the surrounding environment is required for high temperature applications. The development of a continuous Al_2O_3 coating on $SiC_{(P)}/Al_2O_3$ ceramic composite for such protection is achieved using the laser assisted in-situ reaction technique. The as deposited alumina coating was analyzed using optical microscopy and x-ray difractometry. The coated samples were also evaluated for their mechanical properties using three-point bend tests.

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Introduction

The use of high power energy lasers for surface cladding has been acknowledged as a possible method of surface modification for twenty years. A 1976 patent(1) entitled "cladding" involves the use of direct wire feeding under a scanning laser beam. British researchers, however, claim the "shadowing" effect of solid wire does not seem to couple the laser energy as effectively as powder and, hence, powder would be the preferred consumable for surfacing. Powell, for example, has published work using Ni-Cr-Si-B powder fed continuously under a laser beam with a manual powder torch modified to use an argon carrier gas rather than oxy-fuel combustion.(2) Other variations have been devised for direct powder feed into a laser beam (known as direct cladding or cladding).(3~8) Preplacement of powders onto a substrate prior to laser fusing is another possibility instead of attempting to solve problems of "feeding" a powder consumable directly under or in front of an advancing laser beam. Thermal spray methods, such as oxyacetylene flame spray(9) and plasma spray(10~12) have been used to preplace powder onto a substrate for subsequent laser fusing (known as laser sealing).

The direct cladding by laser was obtained by melting a thin layer of substrate and blowing a stream of fine particles of the material which may or may not melt during laser scanning. The direct cladding process produces a metallurgical bonding between cladded layer and substrate. On the other hand, the plasma sprayed layer is primarily mechanically bonded to the substrate. Even after the laser sealing process, this layer still maintains mechanical a bonding with substrate. Hence, the direct cladding layer has much stronger bonding with the substrate than that of laser sealing. This characteristics is very important for obtaining higher corrosion resistance and erosion resistance because of its higher adherence.

Laser cladding has been used successfully to modify surface properties of materials, particularly for improving wear and corrosion resistance (including high temperature). Up to the present time laser cladding has been mainly used on metal surfaces. It appears that no work has been reported on the laser cladding on the ceramic substrate surface.

With the develop of modern industry, ceramic materials applications have been increasingly important and now especially are being considered for high-temperature structural applications, such as heat exchangers, heat turbines, heat engines and magnetohydrodynamic (MHD) generators. Materials used in these systems are exposed to high-temperature corrosive condensed alkali salt environments. SiC, Si_3N_4 and $SiC_{(P)}/Al_2O_3$ currently appear to be leading candidate materials due to their high temperature strength, high thermal conductivity, low thermal expansion and high thermal shock resistance. In particular, SiC particulate-reinforced Al_2O_3-matrix composites have the potential to combine the corrosion resistance of the alumina with the excellent mechanical and thermal properties of silicon carbide. In spite of these unique properties, it has been reported that SiC, Si_3N_4 and SiC/Al_2O_3 were unstable under condensed hot alkali environments.(13~17) It is possible the oxidation rate of silicon ceramics will be accelerated due to the continual removal of the protective layer of SiO_2, for example, by erosion, by dissolution in a glassy coating formed by impinging bed materials, or by the formation of SiO vapor rather than SiO_2. A possible remedy to the corrosion problem is a protective coating on the ceramics.

Few research efforts related to ceramic coatings on ceramics have been reported in the available open literature, partly due to the inherent problems associated with the process. The conventional methods used are chemical vapor deposition, physical vapor deposition, solgel, air spraying and plasma spraying. None of these processes is fully satisfactory because the coatings produced suffer from excessive porosity, inclusions, microcracking, coating segmentation and poor adhesion. This leads to premature cracking, degradation, and failure by internal sulfidation, spallation, reduced mechanical strain, pitting corrosion, condensed salt penetration, and oxygen penetration at high temperature.(18~19) Poor adhesion appears to be the major problem because all of these coatings produced by conventional methods are by mechanical bonding with the substrate.

In several tests where ceramics corroded severely, oxide ceramics corroded substantially less.(20~21) Alumina ceramics were particularly resistant to corrosion because the transport of aluminum and oxygen through alumina is extremely slow compared to transport through most other oxides.(22~24) Thus, the most effective method to develop oxidation resistance in alloys and coatings at high temperatures above 900 °C is to form a continuous layer of alumina.(25~26) The important issues, however, with regard to the effective use of alumina are the development and their adherence to various ceramic substrates.

Laser cladding, a fairly new technique, provides a possibility of an improved method for the deposition of high-quality coatings. Laser cladding offers the following advantages:

- the ability to control dilution and produce ultrafine and/or metastable microstructures;
- the ability to deposit a wide range of materials of high and low melting points;
- the minimal distortion and damage of the underlying substrate;
- the possibility of selectively coating inaccessible and localized areas;
- a rapid deposition rate;
- a metallurgical bonding between the coating and the substrate (the most important aspect).

The objective of this article is to explore the feasibility of laser cladding ceramics on ceramics and it presents preliminary observations and evaluations from a study in laser cladding of Al_2O_3 on the commercially available $SiC_{(P)}/Al_2O_3$ substrate by an in-situ reaction technique.

Experimental Procedures

- Materials

For coating purpose, commercially available $SiC_{(P)}/Al_2O_3$ (equi-volume plus ten volume percent residual free aluminum) composite substrate samples were used. The samples (5 mm x 10 mm x 30 mm coupons) were mechanically polished on the series of grit papers followed by polishing on the cloth wheel with a diamond paste to obtain a mirror finish on the surface. The samples were ultrasonically cleaned in a methanol bath and then thoroughly dried in air.

An approximately 5 micron thick bond layer of titanium was deposited on the $SiC_{(P)}/Al_2O_3$ substrate using PVD prior to the laser treatment. Deposition was carried out on a commercially available Dayton Vacuum unit. Multiple samples were produced simultaneously. In a vacuum of $2x10^{-5}$ Torr, the sample stage was inclined at 45° and was continuously rotated at 30 rpm around the vertical axis. This resulted in the deposite of a uniformly thick bond coat on the surface after five minutes. The current and voltage parameters were 25~30 A and 85~95 V respectively.

- Laser processing

As depicted Figure 1, a dynamic fluidized-bed powder feeder (designed and fabricated in-house), delivered the precursor aluminum powder (4 micron average particle size) at the laser-materials interface region. A pneumatic vibrator in conjunction with a high-pressure air/gas breaks the powder clusters into individual particles by breaking the weak electrostatic force between them. The high-pressure air/gas also fluidizes the powder particles and entrains it to the laser-material interaction region via a delivery tube. An air filter at the top of the powder container avoids excessive pressure build-up while ensuring a continuous and smooth powder delivery rate. Efficient powder delivery can be achieved by selecting a proper combination of the pneumatic vibrator frequency and the inlet gas flow rate. In addition, the inlet gas is also a carrier for the powder and it provides a reactive environment at the laser-material interaction region for conversion of aluminum into an Al_2O_3 ceramic.

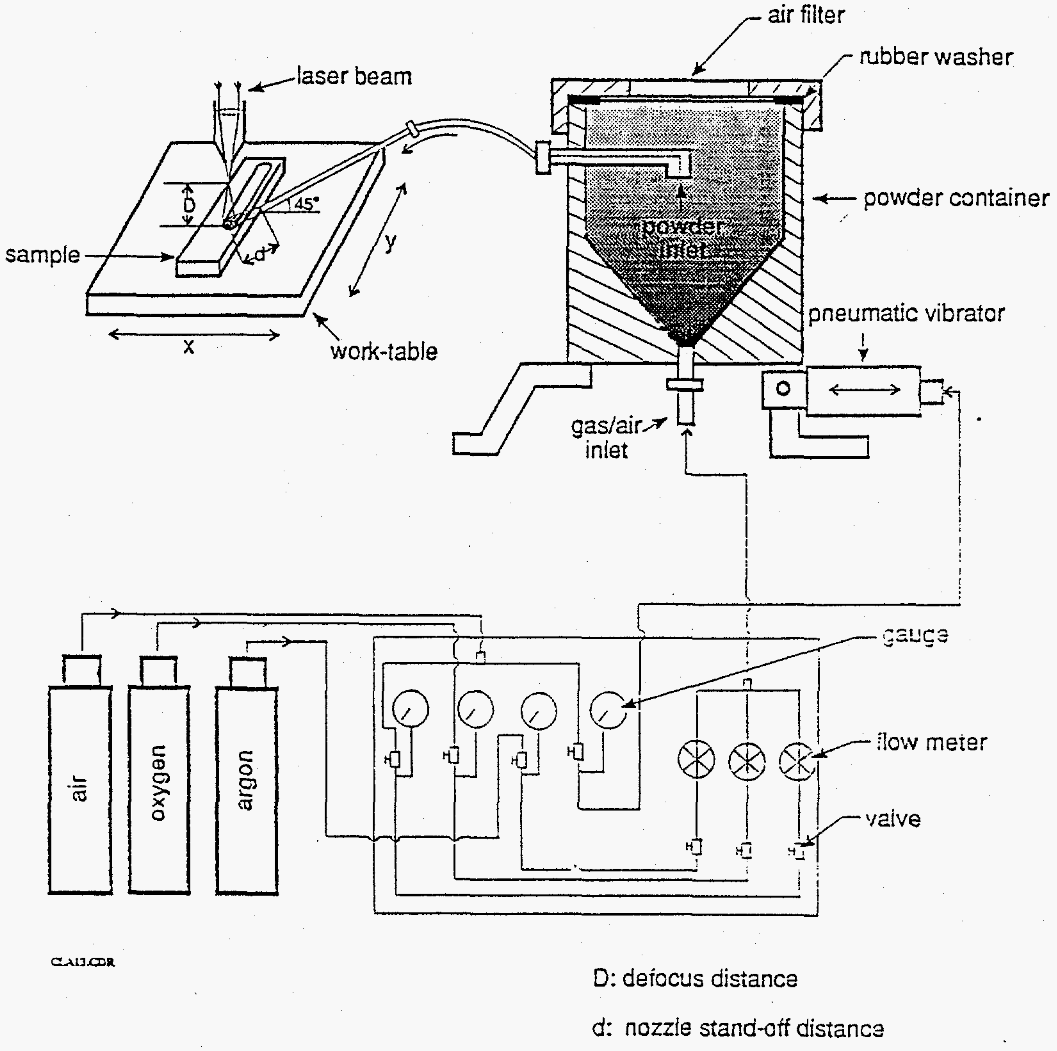

Figure 1. Schematic diagram of the dynamic fluidized-bed powder feeder.

Laser in-situ reaction coating of Al_2O_3 with an aluminum powder was conducted on a titanium bond-coated SiC/Al_2O_3 substrate. A Rofin Sinar RS3000 CO_2 laser (operating in quasi-continuous wave (Q-CW) mode) was employed. The laser beam defocused on the sample surface, which was scanned continuously with some overlap between consecutive passes to cover the entire surface. The laser surface treatment was carried out with a slight overpressure of oxygen. Local heating of the bond-coat, and precursor aluminum powder along with the substrate material created a bond layer at the interface and also converted the aluminum into a ceramic coating. The laser processing parameters are given in Table 1. Microscopic analysis was conducted using optical microscopy and an X-ray diffractometer.

Table 1. Laser Processing Parameters

Delivered power	150 watts
Mode of laser operation	Quasi continuous wave
Beam mode	TEM_{10}
Beam polarization	Circular
Traverse speed	1800 mm/sec
Focal position	8 mm above sample surface
Assist gas	Oxygen, ~1 L/min
Beam overlap	0.85 mm
Surface Bond coat	Ti

- Mechanical Testing

Two sets of strength testing samples were produced from the as-received and laser-induced reaction coated samples. Each set include ten pieces of 5 mm x 10 mm x 30 mm coupons. The mechanical testing performed in this study was not designed to produce an absolute measure value, but rather, to detect any difference in the mechanical properties between the as-received material and laser-treated material (laser induced reaction coated). Because of high thermal shock to the material during laser processing, the purpose of the mechanical testing was to determine any change in the mechanical properties due to laser surface processing. Due to the limitation of small dimensions of available test material, the three-point bend test was employed.

The material supplied for this test was DIMOX™ tube with a 51 mm outside diameter and a wall thickness of approximately 5.0 mm. Lanxide's material designation for this material was 93-X-3015. The sample coupons were cut from the tube, each coupon approximately 30 mm long and 10 mm wide on the outside surface. The inside surface width was less than that of the outside surface. Figure 2 gives sample coupon dimensions. The coupon was roughly considered as rectangular and B {B = (a+b)/2} as its width. Then the bend strength is given by:

$$\sigma = \frac{3PL}{2Bc^2}$$

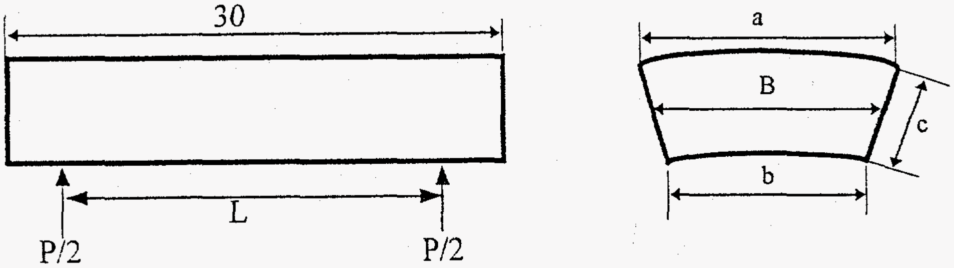

Figure 2. Sample dimensions

Ten of these coupons from each as-received and laser-induced reaction coated samples were selected for bend testing. An Instron testing machine was used. Table 2 gives the parameters used in the three-point bend testing and Table 3 gives the sample dimensions.

Table 2. Parameters Used for Three-point Bend Testing

Load Speed	Normal Load	Record Chart Speed
0.02 in/min	500 lbs	50 in/min

Table 3. Sample Dimensions

Sample	**Sample #**	**a (mm)**	**b (mm)**	**c (mm)**	**B (mm)**
As Received Samples	1	9.94	8.26	4.96	9.10
	2	9.88	7.52	5.08	8.70
	3	9.72	8.84	5.30	9.28
	4	9.52	7.68	4.62	8.60
	5	10.54	8.72	4.96	9.63
	6	9.26	7.62	4.76	8.44
	7	9.34	7.90	5.40	8.62
	8	12.30	9.58	5.04	10.94
	9	9.22	7.26	5.04	8.24
	10	10.80	8.26	5.42	9.53
	Average	10.05	8.16	5.06	9.11
Laser Induced Reaction Coated Samples	1	9.70	8.42	4.80	9.06
	2	10.34	8.48	5.04	9.41
	3	9.70	8.16	4.82	8.93
	4	10.30	8.24	5.40	9.27
	5	10.58	8.64	5.44	9.61
	6	9.80	8.46	5.24	9.13
	7	10.52	8.44	4.94	9.48
	8	10.50	9.26	4.96	9.88
	9	9.80	8.76	5.14	9.28
	10	10.70	9.26	4.80	9.98
	Average	10.19	8.61	5.06	9.40

Results and Discussion

The various combinations of processing and materials parameters were explored to identify the optimum conditions for obtaining a complete coverage and a smooth and adherent coating. It appeared that the use of titanium PVD bond coatings along with the use of conditions mentioned in the Table 1 produced an adherent, relatively smooth and crack-free coating of Al_2O_3 on the $SiC_{(P)}/Al_2O_3$ substrate surface. The marked difference in the surface roughness of as-received and laser induced reaction coating may be seen from the scanning electron micrographs of Fig. 3.

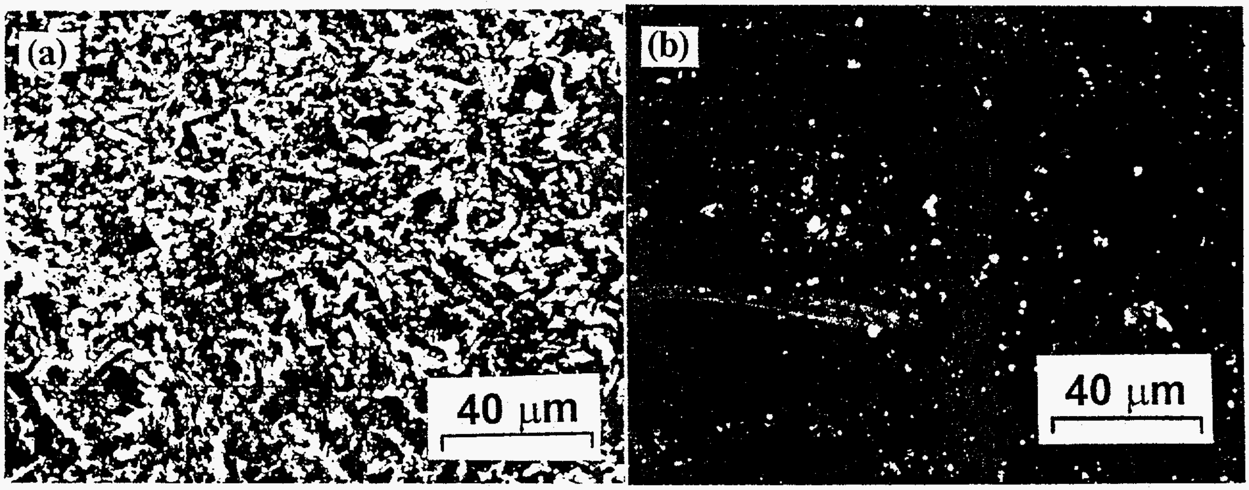

Figure 3. SEM micrograph of plan view, (a) as-received and (b) laser coated

Although there are some micro-cracks within the coating as seen in Fig. 3-b, these cracks are very shallow. A few of them penetrate further into the coatings as illustrated in the Fig. 4. A cross-sectional view (Fig. 4) indicates a defect free interface and the coating appeared

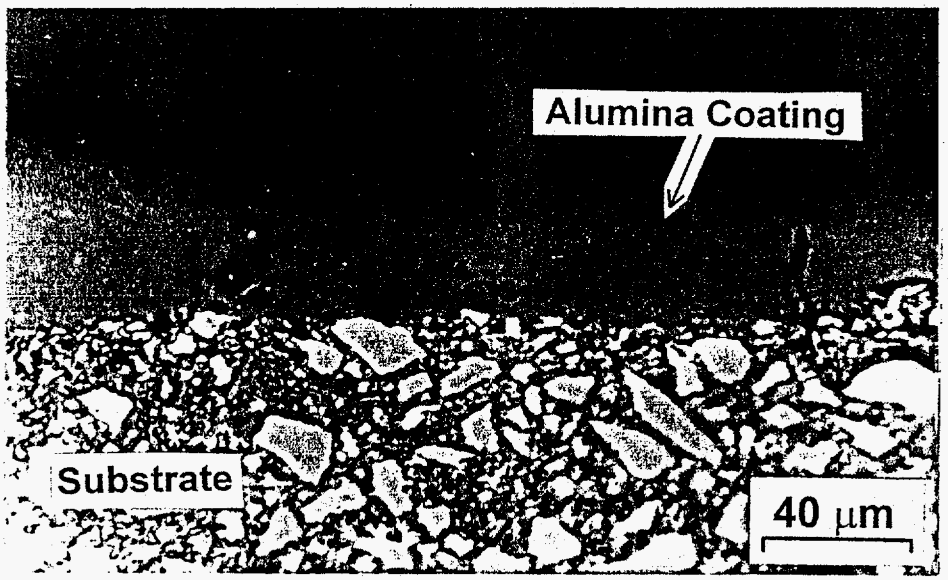

Figure 4. Cross-sectional view of the laser-induced reaction-coated SiC/Al_2O_3

uniform with limited amount of porosity. The laser induced transformation of the aluminum powder into the required ceramic coating was confirmed by using x-ray diffraction. Figure 5 shows the x-ray diffraction analysis of the laser-induced reaction transformed coating on the $SiC_{(P)}/Al_2O_3$. The x-ray spectrum indicates the existence of Al_2O_3 peaks and the absence of any other phase within the sensitivity of the instrument.

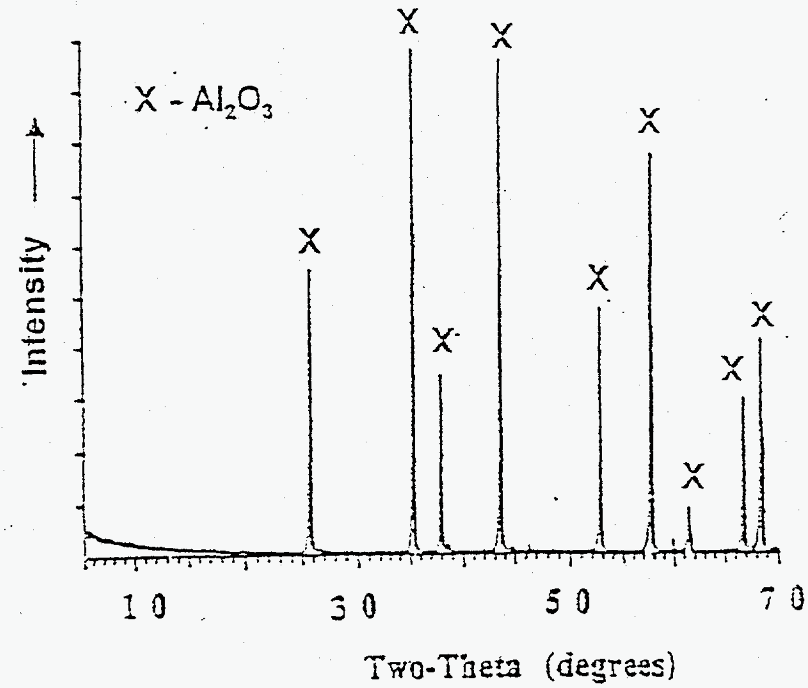

Figure 5. X-ray diffraction analysis of laser-induced reaction-coated $SiC_{(P)}/Al_2O_3$

Rippling effects on the surface of the laser coating were observed as illustrated in Fig. 3-b. The main rippling effect is perpendicular to the traverse direction. Similar features have been studied in detail by various researchers(26, 27) for a variety of metallic alloys subjected laser surface melting. The phenomena involved are complex, and depend on the surface tension driven flow and resonant wave length of the melt pool. This activity is essentially a function of the temperature of the surface tension. This may explain differences between the rippling in metals and the laser ceramics coating. The ripples in metals have a herring bone formation with respect to the traverse direction, whereas in the case of the laser deposited ceramic coating they are nearly perpendicular. This may be a consequence of the low thermal conductivity of the ceramic and the fact that, unlike most metals, the conductivity of alumina is effectively invariant with temperature. These characteristics of the conductivity will affect the temperature gradient, and hence surface tension differences.

Table 4 is the summary of the results of mechanical testing. As seen in Table 5, the reduction of about 14% in the strength of the laser coated sample compared to the as-received sample is realized. Such reduction may be due to a single or combination of factors such as thickness of the coating, physical characteristics (porosity and cracks) of the interface between the coating and the substrate, soundness of the coating (pores, cracks and inclusions), surface topography of the coating (roughness cracks and pores) and chemical phases at the interface between the coating and the substrate. The evaluation of the relative strength provides a tool to choose combination of materials and processing parameters at optimum level for the production of sound and strong coatings.

Table 4. Three Point Bend Test Results

Sample	**Sample #**	**Fracture Load P (lbs)**	**σ (Kpsi)**	**σ (MPa)**
As Received Samples	1	322	31.49	217.13
	2	366	35.75	246.48
	3	360	30.28	208.81
	4	338	40.35	278.25
	5	408	37.76	260.39
	6	291	33.37	230.09
	7	496	43.23	298.06
	8	400	31.56	217.58
	9	324	33.94	234.05
	10	474	37.13	256.00
Laser Induced Reaction Coated Samples	1	275	28.84	198.83
	2	315	28.90	199.26
	3	381	40.27	277.67
	4	468	37.97	261.78
	5	422	32.50	224.09
	6	294	25.72	177.32
	7	288	27.30	188.23
	8	288	25.98	179.15
	9	323	28.85	198.89
	10	286	27.23	187.74

Table 5. Summary of Three-point Bend Test Results

Sample	Average σ (Mpa)	Relative Value
As-received Samples	244.68	1
Laser Induced Reaction Coating Samples	209.30	0.86

Summary

An alumina coating of about 100 micron thickness was deposited on $SiC_{(P)}/Al_2O_3$ substrate using a laser assisted in-situ reaction technique. The coating appeared to be adherent to the substrate and free of cracks and porosity, although a few surface microcracks were observed. X-ray diffraction analysis indicated that the entire coating was alumina. The evaluation of the coated samples in comparison with the as-received samples based on three-point bending test results indicated a strength reduction of about 14%.

Acknowledgements

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References

1. D. S. Gnanamuthu, "Cladding", US Patent 3942180, April 20, 1976.

2. J. Powell and W. M. Steen, "Vibro Laser Cladding", Laser in Metallurgy, edited by K. Mukherjee and J. Mazumder, Conference Proceedings published by the Metallurgical Society of AIME (1981).

3. J. D. Ayers, R. J. Schaefer, and W. P. Robey, " A Laser Processing Technique for Improving the Wear Resistance of Metals", Journal of Metals, August, 1981.

4. D. Crucian, G. Molino, M. Musci, E. Borsella and R. Fantoni, "Applications of Laser for Ceramic Alloy on Metallic Surface", IL NUOVO CIMENTO, Vol. 11D, No. 3, pp. 495-502 (1989)

5. E. Vandehaar, P. A. Molian, and M. Baldwin, "Laser Cladding of Thermal Barrier Coatings", Surface Engineering, Vol. 4, No. 2, pp. 159-172 (1990)

6. E. Ramous, L. Giordano, A. Tiziani, B. Badan and M. Cantello, "Laser Cladding of Ceramic and Metallurgic Coatings on Steel", Key Engineering Materials, Vol. 46, pp. 425-434 (1990)

7. K. M. Jasim, R. D. Rawlings, D. R. F. West, "Thermal Barrier Coatings Produced by Laser Cladding", J. of Materials Science, Vol. 25, pp. 4943-4948 (1990)

8. W. M. Steen, R. M. Vilar, K. G. Watkins, M. G. S. Fereira "Alloy System Analysis by Laser Cladding", Proceedings of the Laser Materials Processing Symposium, pp. 278-287, ICALEO'1992

9. G. C. Irons, "Laser Fusing of Flame Spray Coatings", Welding Journal Research Supplement, December 1978

10. J. D. Ayers and R. J. Schaefer, "Consolidation of Plasma Sprayed Coating by Laser Remelting", SPIE Vol. 198 Laser Applications in Materials Processing, (1979)

11. Nobuya Iwamato and Norimasa Umesaki, "Surface Treatment of Plasma-sprayed Ceramic Coatings by a Laser Beam", Surface and Coatings Technology, Vol. 34, pp.59-67 (1988)

12. L. Mannik, A. V. Manolescu, J. O. Noga, S. K. Brown and A. G. McMillan, "Laser Modified Coatings for Energy Systems", Proceedings of the Laser Materials Processing Symposium, pp. 237-250, ICALEO'1992

13. J. L. Smialek and N. S. Jacobson, "Mechanism of Strength Degradation for Hot Corrosion of α-SiC", J. Am. Cerm. Soc. Vol. 69, No. 10, pp. 741-752 (1986)

14, M. Shimada, T. Sato, Y. Koike and T. Endo, "Corrosion and Degradation in Strength of Silicon Nitride Based Ceramics by Alkali Surface and Carbonate Melts", Adv. Mats. Vol. 4, Materials Research Society (1989)

15. N. S. Jacobson, J. L. Smialek and D. S. Fox, " Molten Salt Corrosion of Ceramics", Corrosion of Advanced Ceramics, edited by K. G. Nickel Kluwer, Academic Publishers (1993)

16. A. Gadalla, M. Elmasry, P. Kongkachuichay, " High Temperature Reactions within SiC - Al_2O_3 Composites," *Journal of Materials Research,* Vol. 7 No. 9, pp. 2585-2592 (1992)

17. W. Kern, R. E. Tressler and M. J. Mcnallan, "Durability of SiC/Al_2O_3 Composites in Contact with Sodium Silicate," *News letter, Center for Advanced Materials,* Penn. State Univ. (1992)

18. J. Schienl, and J. Smyth, "High Temperature Coating Study to Reduce Contact Stress Damage of Ceramics," *ORNL/Sub/84-47992/1*, Oak Ridge National Laboratory, Oak Ridge, Tennessee, (March 1987)

19. J. I. Federer, "An Investigation of Ceramic Coating for Protection of SiC from High Temperature Corrosion," Oak Ridge National Laboratory, Oak Ridge, Tennessee, (1990)

20. J. I. Federer and P. J. Jones, "Oxidation/Corrosion of Metallic and Ceramic Materials in an Aluminum Remelt Furnace," *ORNL/TM-9741*, Oak Ridge National Laboratory, Oak Ridge, Tennessee, (December 1985b)

21. J. I. Federer, 1st Int. Ceramics Science & Technology Congress, Anaheim, CA, 1989, paper no. 27-SXV-89C

22. N Birks, G. H. Meier and F. S. Pettit, "Forming Continuous Alumina Scales to Protect Superalloys," *JOM*, vol. 46, no. 12, pp. 42-46 (1994)

23. W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics* 2nd ed., pp. 240, John Wiley & Sons, Inc., New York (1976)

24. J. L. Smialek and G. H. Meier, "High Temperature Oxidation," *Superalloys II*, ed. C. T. Sims, N. S. Stoloff, W. C. Hagel, pp. 295, New York, NY: John Wiley and Sons (1987)

25. G. C. Wood, *Oxidation of Metals and Alloys* pp. 201 Metal Park, OH: ASM (1971)

26. J. I. Federer, "An Investigation of Ceramic Coating for Protection of SiC from High Temperature Corrosion," Oak Ridge National Laboratory, Oak Ridge, Tennessee (1990)

27. T. R. Anthony and H. E. Cline, "Surface rippling induced by surface tension gradients during laser surface melting," J. Appl. Phys., 48(1977)3888-3894

28. I. C. Hawkes, M. Lamb, W. M. Steen and D. R. F. West, "Surface topography and fluid flow in laser surface melting," (Proc. 3rd CISFEL Conf, Lyon, France, Sept. 1983), 125-131

KEY WORDS:

alumina	1, 2, 3, 4, 8, 10
CO_2 laser	4
cladding	2, 3
powder	2, 3, 4
three-point bend test	1, 5, 6, 9, 10
oxidation	2
adherence	2, 10
bond coat/layer	3, 4, 7
laser induced	1, 5, 6, 7, 8, 9