

Augmentation of the mechanical and chemical resistance characteristics of an Al₂O₃-based refractory by means of high power diode laser surface treatment

J. Lawrence* and L. Li**

*Manufacturing Engineering Division, School of Mechanical & Production Engineering, Nanyang Technological University (NTU), Nanyang Avenue, Singapore 639798.

**Laser Processing Research Centre, Department of Mechanical, Aerospace and Manufacturing Engineering, University of Manchester Institute of Science and Technology (UMIST), Manchester, M60 1QD, UK.

Correspondence

Dr. Jonathan Lawrence
Manufacturing Engineering Division,
School of Mechanical & Production Engineering,
Nanyang Technological University (NTU),
Nanyang Avenue,
Singapore 639798.

Tel : (+65) 790 5542

Fax : (+65) 791 1859

email : mjlawrence@ntu.edu.sg

Abstract

Augmentation of the wear rate and wear life characteristics of an Al_2O_3 -based refractory within both normal and corrosive (NaOH and HNO_3) environmental conditions was effected by means of high power diode laser (HPDL) surface treatment. Life assessment testing revealed that the HPDL generated glaze increased the wear life of the Al_2O_3 -based refractory by 1.27 to 13.44 times depending upon the environmental conditions. Such improvements are attributed to the fact that after laser treatment, the microstructure of the Al_2O_3 -based refractory was altered from a porous, randomly ordered structure, to a much more dense and consolidated structure that contained fewer cracks and porosities. In a world economy that is increasingly placing more importance on material conservation, a technique of this kind for delaying the unavoidable erosion (wear) and corrosion that materials such as the Al_2O_3 -based refractory must face may provide an economically attractive option for contemporary engineers.

Keywords: High power diode laser (HPDL); Refractory; Surface glazing; Erosion; Wear; Corrosion; Life characteristics

1. Introduction

Environmental issues bring to the fore the need for engineers to make material conservation a matter of high importance. Erosion (wear) and corrosion are known causes of a considerable amount of wastage in many high temperature applications where materials such as refractories are employed. Therefore, any means by which the life of the refractory could be extended would be economically advantageous. The physical and chemical stability at high temperatures of refractory materials means that they find wide usage in application areas such as linings for furnaces and incinerators. Such operating environments demand that the linings must withstand mechanical wear and chemical attack from the movement of heated solids, liquids and/or gasses [1], as well as providing the optimum amount of heat insulation [2]. This creates a dilemma for engineers working in this field since porous refractories will act as effective insulators because porosity is inversely proportional to thermal conductivity [3], but will be susceptible to penetration by corrosive reagents during operation on account of their open structure. Consequently the need arises to employ denser refractories which degrade less due to their more closely packed structure [4]. Clearly, neither solution is ideal and so the protection of refractories exposed to aggressive high temperature environments generally depends on the formation of an effective diffusion barrier layer which possesses superior erosion and corrosion properties to the bulk. Existing methods for providing improved erosion and corrosion protection for refractories are based either on tailoring the manufacturing process or using a coating. Typically, tailoring of the manufacturing process involves techniques for densification of the refractory material [2]. As for coatings, established technologies using chemical, mechanical and/or thermal methods are employed to apply surface layers [5, 6]. However, problems such as residual stress generation, low production rates, coating stability, microcracking and porosity are often attendant with these methods [7, 8].

It is a distinct possibility that the technology of laser materials processing may offer a viable alternative to the existing methods for improving the erosion and corrosion resistance of refractories. Moreover, many of the disadvantages associated with the existing methods may be eliminated due to the operating characteristics of laser technology. However, despite this, investigations into the laser processing of refractories are few in number. Work by Bradley et al. examined the surface treatment of alumina-based refractories with CO₂ and HPDLs [9, 10] and a xenon arc lamp [11], whilst Lawrence and Li [12] studied the laser beam interaction characteristics of the Al₂O₃-based refractory considered in this work. In contrast, several successful studies have shown the feasibility of using lasers to improve the surface characteristics of various ceramic and composite materials. The remelting of ZrO₂-based protective ceramic layers using a CO₂ laser [13] was shown to result in a marked decrease in the level of structural defects. Further, the CO₂ laser remelting of a number of oxide ceramic coatings has been found to effect significant improvements in corrosion resistance

[14], whilst the CO₂ laser remelting of Al₂O₃ and Al₂O₃-TiO₂ coatings yielded an increase in hardness and wear resistance [15]. After excimer laser treatment of the surface of Al₂O₃, Cappelli et al. [16] noted changes in the surface chemistry and morphology of the material, whilst Wu et al. [17] found that excimer laser treatment of Al₂O₃-SiC occasioned surface smoothing and an increase in the toughness of the material. The surface glazing of mullite with a HPDL by Schmidt and Li [18] resulted in a glaze that exhibited good adherence to the bulk ceramic but was severely cracked. To date, many studies have been carried out to investigate the laser surface processing of concrete. As part of nuclear plant decommissioning, Li et al. [19-22] conducted research to determine the workability of several laser techniques for sealing/fixing radioactive contamination onto concrete surfaces. Work by Sugimoto et al. [23] and Wignarajah et al. [24] focused upon modifying the surface appearance and surface properties of cement based materials using a high power CO₂ laser. Borodina et al. [25] has carried out investigations into the structural changes within the composition of zirconia concrete caused by surface exposure to CO₂ laser radiation. More detailed and comprehensive studies conducted by Lawrence and Li have investigated the feasibility and characteristics of HPDL generated glazes on the ordinary Portland cement (OPC) surface of concrete [26, 27]. In further work Lawrence and Li carried out a comparison of the glazes generated with both CO₂ and HPDL's [28, 29].

This present work is concerned with examining and quantifying the wear characteristics of a glaze generated on the surface of an Al₂O₃-based refractory by means of high power diode laser (HPDL) radiation. This is of particular interest since the inherent compact and robust nature of the HPDL enables it to be portable. Other industrial lasers only allow the workpiece to be processed at a dedicated laser work station, whereas on the other hand, the HPDL can be used for on-site processing.

2. Experimental procedures

The material used in the experiments was an Al₂O₃-based refractory containing various impurities. The composition by weight of the refractory is as follows: Al₂O₃ (83.5%), SiO₂ (9%), Cr₂O₃ (4.5%), P₂O₅ (1.6%), Fe₂O₃ (0.4%), TiO₂ (0.3%), MgO (0.3%), NaO₂ (0.2%), CaO (0.1%) and K₂O (0.1%). The refractory material studied is used commercially as a lining in industrial furnaces and incinerators. The refractory was obtained (from Cleanaway) in the form of blocks (200 x 200 x 100 mm³). The as-received blocks typically contained 12% porosity with aggregates of 1 to 3 mm in size being evenly distributed throughout the bricks. Furthermore, small sized cracks and porosities were generally visible on the surfaces of the as-received samples. For the purpose of experimental convenience the as-received refractory blocks were sectioned into small cubes (20 x 20 x 10 mm³)

with only two-thirds being laser treated. The selected refractory samples were treated with both lasers at room temperature and in normal atmospheric conditions.

A HPDL (Diomed, D120) emitting at 810 ± 20 nm with a maximum output power of 120 W was used in this work. The beam was delivered to the work area by means of a 4 m long, 1 mm core diameter optical fibre, the end of which was connected to a 2:1 focusing lens assembly. The laser operated in the continuous wave (CW) mode and produced a multi-mode beam. The defocused HPDL beam was fired across the surface of the as-received Al_2O_3 -based refractory samples by traversing the samples beneath the beam using the x- and y-axis of 3-axis computerised numerical control (CNC) gantry table. In order to protect the laser optics a coaxially blown O_2 shield gas jet at a rate of 10 l/min was used. Further characterisation of the HPDL generated glazes was carried out using optical microscopy, scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and X-ray diffraction (XRD) techniques.

To determine the wear resistance characteristics of the HPDL generated glazes on the surface of the Al_2O_3 -based refractory, and also those of the as-received surface, wear tests were conducted in accordance with Fig. 1. All the samples, as-received and laser treated, were weighed and then clamped individually in the vice of a common shaping machine. A steel abrader was attached to the floating head of the shaping machine and moved cyclically back and forth across the as-received and laser glazed Al_2O_3 -based refractory surfaces. The total distance moved in one cycle was 6 mm while the traverse speed was 180 mm/min. By applying weights to the floating head a frictional force of 60 N was generated. The samples were subjected to the frictional force for 8 h, being removed from the machine and weighed at 2 h intervals.

3. Results

The resistance of any material to wear is related primarily to the hardness of the material in comparison with the that of other materials with which it comes into contact [30]. However, wear resistance is not directly proportional to hardness, nor does it always increase with hardness [31]. Fig. 2 shows the relationship between weight loss and the friction time for the HPDL generated glaze and that of the as-received Al_2O_3 -based refractory surface. As is clear from Fig. 2 that the wear resistance of HPDL generated glaze effected a considerable increase in wear resistance over the as-received surface, with the weight loss being approximately 1.5 times lower after 4 h, and 3 times lower after 8 h.

To ascertain what effect the HPDL generated glaze had on the corrosion resistance of the Al_2O_3 -based refractory in comparison with that of the as-received surface, corrosion resistance tests based on BS 6431 [32] were conducted using nitric acid (HNO_3) and sodium hydroxide (NaOH). The

experiments were carried out by dropping small amounts of the corrosive agents, in the concentration ratios of 80%, 60%, 40%, 20% and 10%, on to the as-received and laser glazed surfaces of the Al₂O₃-based refractory at hourly intervals for 4 h. Thereafter the samples were examined optically and subjected to the mechanical wear test described earlier (see Fig. 1). It is worth mentioning that high concentrations of the corrosive agents were used simply to accelerate the tests.

Both reagents in the concentrations 80% and 60% were seen to attack immediately the as-received surface of the Al₂O₃-based refractory with a similar degree of severity. In marked contrast, the HPDL glazed surface displayed no discernible change in either morphology or microstructure. The variation in wear resistance of the as-received surface of the Al₂O₃-based refractory when exposed to the reagents with an 80% concentration is shown in Fig. 3. As is evident from Fig. 3, the wear resistance of the refractory is significantly affected when exposed to a corrosive environment. As one can see, the weight loss of the as-received sample was approximately 4 times higher than the HPDL treated surface after 4 h and approximately 10 times higher after 8 h for the HNO₃. In the case of the NaOH, the weight loss was slightly less after both 4 and 8 h. Conversely, only a marginal increase in the wear rate was observed for the HPDL glazed surface as Table 1 shows.

4. Discussion

From the results of the wear tests it is clear that the wear resistance characteristics of the Al₂O₃-based refractory are greatly improved after surface glazing with the HPDL. This improvement in wear rate was especially evident when the tests were conducted in corrosive environments. The distinct difference in wear rate between the HPDL treated and as-received surface, in both normal and corrosive environments, can be ascribed totally to the different surface structures. In the as-received condition, the surface of the Al₂O₃-based refractory consists of a porous, randomly ordered structure, whereas the HPDL glazed surface consists of a much more dense and consolidated structure that contains fewer cracks and porosities. Also, it was noted that the HPDL generated glazes were much harder than the as-received surface of the Al₂O₃-based refractory, having a respective value of around 6 compared to 2 on the Mohs scale. Such significant alterations in the nature of the surface of the Al₂O₃-based refractory will naturally afford the HPDL generated glaze better wear resistance over an as-received surface. In addition to the improvements in the wear resistance of the Al₂O₃-based refractory realised after HPDL surface treatment, a marked difference in the corrosion resistance of the material was observed after laser treatment also. Again, due to the much more dense and consolidated structure of the laser generated glaze, coupled with the fact that it contains fewer porosities, the glaze will therefore possess a greater resistance to corrosive reagents than the porous structure of the as received surface of the Al₂O₃-based refractory.

Based on the findings that reveal that the wear and corrosion characteristics of HPDL generated glaze exceed those of the as-received Al₂O₃-based refractory surface, it would be natural to assume that the life characteristics of the HPDL laser glaze may also surpass those of the as-received Al₂O₃-based refractory. However, in any analysis of the wear life of the two materials, the in-situ relative thickness of the HPDL treated and the as-received Al₂O₃-based refractory surface must be considered in order to give a true interpretation of the actual life characteristics. This is especially the case when considering the wear resistance (with and without exposure to corrosive chemical agents). Thus the increase in wear life can be given by

$$\text{Increase in wear life} = \frac{\text{Laser glaze wear life}}{\text{Untreated OPC wear life}} \quad (1)$$

where,

$$\text{Wear life} = \frac{\text{Density} \cdot \text{Thickness}}{\text{Wear rate}} \quad (1a)$$

The wear rate details and the nominal life increase of the HPDL generated glaze over the as-received Al₂O₃-based refractory surface are given in Table 1. As one can see from Table 1, an increase in the wear life of the Al₂O₃-based refractory was occasioned after HPDL treatment regardless of the environment. In particular, it can be seen that the increase in wear life of the HPDL generated glaze over the as-received Al₂O₃-based refractory surface varied markedly depending on the working environment, perhaps expectedly becoming more pronounced in the corrosive conditions.

4. Conclusions

Marked improvements in the wear and corrosion characteristics of an Al₂O₃-based refractory were observed after surface treatment with a HPDL. What is more, the HPDL generated surface glaze was found to effect an increase in the wear life of the Al₂O₃-based refractory in both normal and corrosive (NaOH and HNO₃) environmental conditions. Under normal conditions the wear rate of the as-received Al₂O₃-based refractory surface was 7.13 mg/cm²/h¹, increasing dramatically to 51.25 mg/cm²/h¹ and 78.75 mg/cm²/h¹ when exposed to NaOH and HNO₃ respectively. In contrast, only very minor increases in the wear rate were experienced by the HPDL treated surface when tested in the corrosive environments, increasing from 2.38 mg/cm²/h¹ under normal conditions to 2.43 mg/cm²/h¹ and 2.49 mg/cm²/h¹ when exposed to NaOH and HNO₃ respectively. Life assessment testing revealed that the HPDL generated glaze increased the wear life of the Al₂O₃-based refractory by 1.27 to 13.44 times depending upon the environment. It is asserted that the observed improvements in the wear rate and wear life of the Al₂O₃-based refractory after HPDL surface treatment are due to the generation of a surface with improved morphology and microstructure which

was more resistant to wear in normal and corrosive environments. More specifically, the improvements can be attributed to the fact that after HPDL treatment, the microstructure of the Al₂O₃-based refractory was altered from a porous, randomly ordered structure, to a much more dense and consolidated structure that contained fewer cracks and porosities. It is believed that considerable economic and material benefits could be realised from the deployment of the HPDL-based technique for generating effective and efficient coatings on the surface of the Al₂O₃-based refractory.

References

1. W.R. Niessen, Combustion and incineration processes, Dekker, New York (1978).
2. J.D. Gilchrest, Fuels, furnaces and refractories, Pergamon, London (1977).
3. K. Shaw, Refractories and their uses, Applied Science Publishers, London (1972).
4. S. Dellaire, R. Angers, J. Can. Ceram. Soc. 51 (1982) 29-37.
5. J. Pou, P. Gonzalez, E. Garcia, D. Fernandez, J. Serra, B. Leon, S.R.J. Saunders, M. Perez-Amor, Appl. Surf. Sci. 79/80 (1994) 338-343.
6. P. Lambert, B. Marple, B. Arsenault, Proc. Int. Symp. on Developments and Application of Ceramics and New Metal Alloys, Toronto, Canada, (1993) 515-525 (Canadian Institute of Mining, Toronto).
7. Y.G. Gogotsi, V.A. Lavrenko, Corrosion of high performance ceramics, Springer, Berlin (1992).
8. W. Weitoa, R. Streiff, W. Maocai, Mater. Sci. Eng. A 121 (1989) 499-507.
9. L. Bradley, L. Li, F.H. Stott, Appl. Surf. Sci. 138/139 (1999) 233-239.
10. L. Bradley, L. Li, F.H. Stott, Mater. Sci. Eng. A, 278 (2000) 204-212.
11. L. Bradley, L. Li, F.H. Stott, Appl. Surf. Sci. 154/155 (2000) 675-681.
12. J. Lawrence, L. Li, Appl. Surf. Sci. 168 (2001) 71-74.
13. Adamski, R. McPherson, Proc. 11th Int. Thermal Spraying Conf. New York, USA, (1986) 555-564 (ASME, New York).
14. K. Kobylanska-Szkaradek, Lasers in Eng. 9 (1999) 127-138.
15. Y.Z. Yang, Y.L. Zhu, Z.Y. Liu, Y.Z. Chuang, Mater. Sci. Eng. A, 291 (2000) 168-172.
16. E. Capelli, S. Orlando, D. Sciti, M. Montozzi, L. Pandolfi, Appl. Surf. Sci. 154 (2000) 682-688.
17. Y.N. Wu, Z.C. Feng, J. Liang, J. Mater. Sci. Tech. 16 (2000) 401-404.
18. M.J.J. Schmidt, L. Li, Appl. Surf. Sci. 168 (2000) 9-12.
19. L. Li, P.J. Modern, W.M. Steen, Proc. LAMP '92, Nagaoka, Japan, (1992) 843-848 (High Temperature Society of Japan, Osaka).
20. L. Li, W.M. Steen, P.J. Modern, Proc. ISLOE '93, Singapore, (1994) 25-30 National University of Singapore, Singapore).
21. L. Li, W.M. Steen, P.J. Modern, J.T. Spencer, Proc. RECOD '94, London, UK, (1994) 24-28 (SPIE, Bellingham).

22. L. Li, W.M. Steen, P.J. Modern, J.T. Spencer, Proceedings of EUROPTO '94: Laser Materials Processing and Machining, Frankfurt, Germany, (1994) 84-95 (SPIE, Bellingham).
23. K. Sugimoto, S. Wignarajah, K. Nagasi, S. Yasu, Proc. ICALEO '90, Boston, USA, (1991) Vol. 71, 302-312 (Laser Institute of America, Orlando).
24. S. Wignarajah, K. Sugimoto, K. Nagai, Proc. ICALEO '92: Laser Materials Processing, Orlando, USA, (1993) Vol. 75, 383-393 (Laser Institute of America, Orlando).
25. T.I. Borodina, G.E. Valyano, N.I. Ibragimov, E.P. Pakhomov, A.I. Romanov, L.G. Smirnova, P.K. Khabibulaev, J. Phys. Chem. Mater. Treatment, 25 (1995) 541-546.
26. J. Lawrence, L. Li, Optics Laser Tech. 31 (2000) 583-591.
27. J. Lawrence, L. Li, J. Laser Apps. 71 (2000) 1-8.
28. J. Lawrence, L. Li, Mater. Sci. Eng. A, 284 (2000) 93-102.
29. J. Lawrence, L. Li, Mater. Sci. Eng. A, 287 (2000) 25-29.
30. H. Dickson, Glass: A Handbook for Students and Technicians, Hutchinsons Scientific and Technical Publications, London, 1951.
31. B. Petitbon, L. Boquet, D. Delsart, Laser surface sealing and strengthening of zirconia coatings, Surf. & Coat. Tech. 49 1991 57-61.
32. BS 6431: Part 19: 1984, Ceramic Wall and Floor Tiles: Method for Determination of Chemical Resistance. Glazed Tiles.

List of Figures

Fig. 1. Schematic illustration of the experimental set-up for the wear tests.

Fig. 2. Relationship between weight loss and friction time for the as-received and HPDL treated Al_2O_3 -based refractory.

Fig. 3. Relationship between weight loss and friction time for the as-received Al_2O_3 -based refractory with different reagent types at the maximum concentration (80%).

Fig. 4. Typical high magnification SEM plan view of the HPDL generated glaze on Al_2O_3 -based refractory surface.

Fig. 5. Typical low magnification SEM cross-sectional view of the HPDL generated glaze on Al_2O_3 -based refractory surface.

Fig. 1

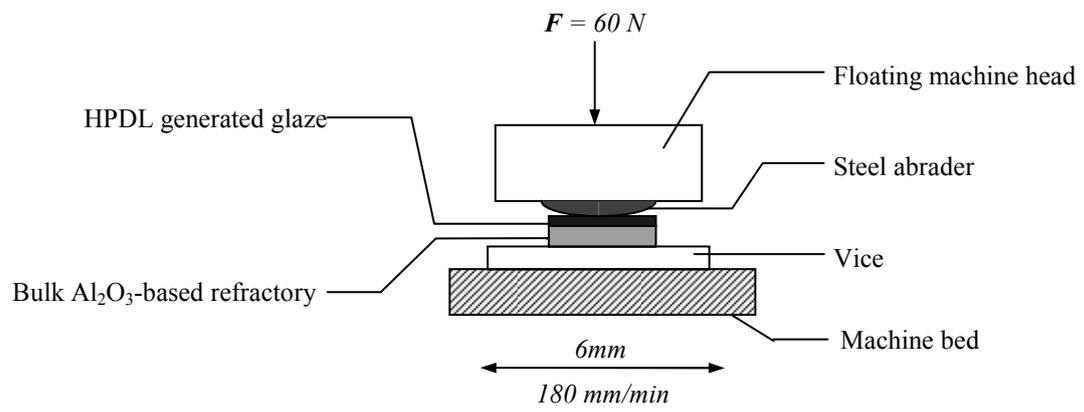


Fig. 2

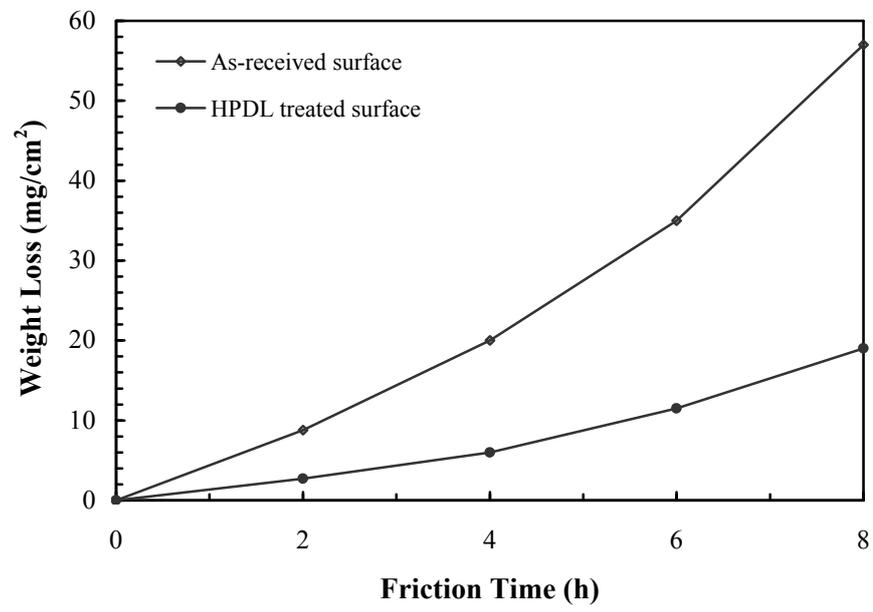


Fig. 3

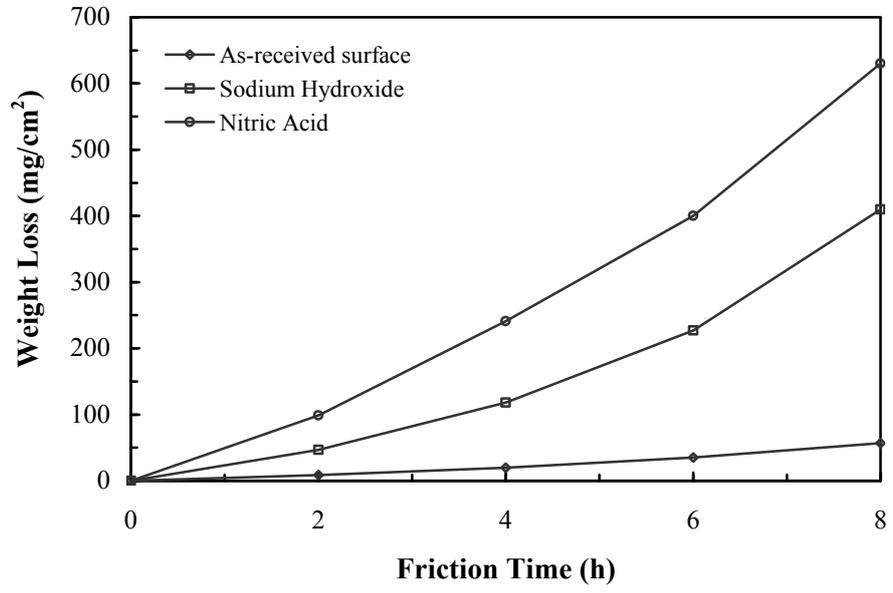


Fig. 4

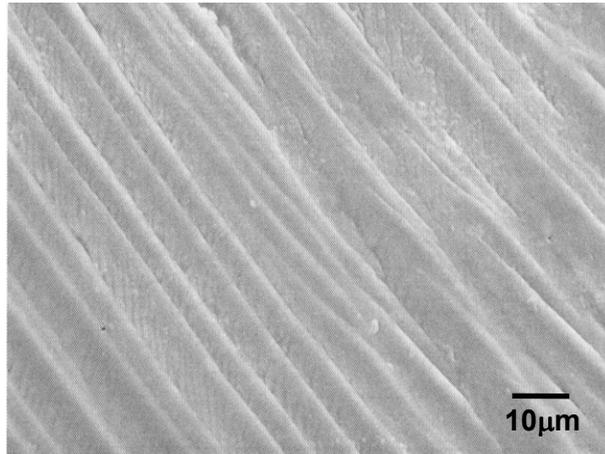
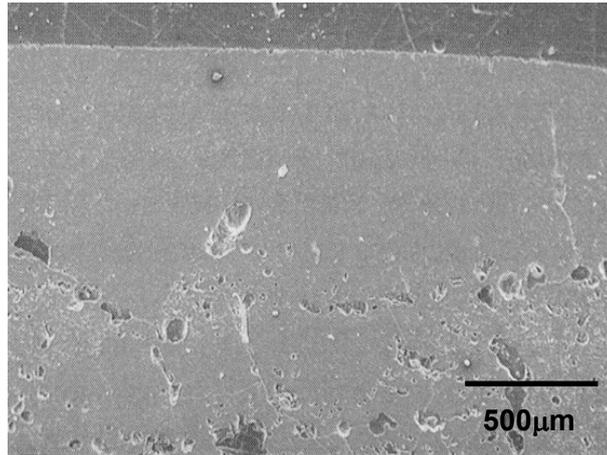


Fig. 5



List of tables

Table 1. Wear rate details and the nominal life increase of the HPDL generated glaze over the as-received Al₂O₃-based refractory in normal and corrosive environments.

Table 1.

	Density	Thickness	<u>Wear Rate (mg/cm²/h¹)</u>		
			Unexposed	NaOH	HNO ₃
As-received surface	2450 (kg/m ³)	1.75 (mm)	7.13	51.25	78.75
HPDL treated surface	2600 (kg/m ³)	0.70 (mm)	2.38	2.43	2.49
Increase in Wear Life	~	~	1.27	8.95	13.44