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The direct bonding between copper and MgO-doped Si_3N_4

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An application of direct bonding method for copper to silicon nitride (Si_3N_4) joining was investigated. Si_3N_4 was sintered with 5 wt% MgO at 1700°C for 30 min in nitrogen atmosphere, and oxidized at various temperatures. The bonding was performed at 1075° C in nitrogen atmosphere with low oxygen partial pressure. The direct bonding was not achieved for the Si_3N_4 oxidized below 1200° C or nonoxidized. During oxidation, magnesium ion added as sintering aids, diffused out to the surface of Si_3N_4 and formed $MgSiO_3$, which seemed to have an important role in the bonding. Fracture of the bonded specimen under tensile stress took place within the oxide layer of Si_3N_4. The bonding strength was decreased with oxidation temperature and time. Maximum strength was found to be 106 kg cm^{-2} for the Si_3N_4 oxidized at 1200° C for 1 h.

1. Introduction

Silicon nitride (Si_3N_4) is one of the candidate materials for the high temperature structural components with its remarkable features such as high strength, high hardness, good resistance to wear, light weight, etc. [1-3]. Such applications of Si_3N_4 ceramics require reliable bonding methods with metallic components.

Until now, several methods have been developed for ceramic to metal bonding; Mo-Mn process, molyoxide process, ceramic frit process, solid state process and active metal process [4-8]. Of these methods, the studies on sintered Si_3N_4 to metal bonding have mostly concentrated on the solid state process [9, 10] and active metal process [11-13]. But their limitations of practical application have made it necessary to develop new techniques for Si_3N_4 to metal bonding [14].

Direct bonding (DB) technique is a new bonding method using eutectic melt from the reaction between gas and metal [15]. Neither filler material nor pressure is needed in this bonding method. So the DB method has been considered more useful than other methods for bonding of components with complex shape. But its application has been successful only for oxide ceramics to metal bonding [16-19]. Several studies have been interested in the bonding between nonoxide ceramics and metal by the DB method [20, 21].

Recently, Tanaka *et al.* [21] reported that the direct bonding between 5 wt% Y_2O_3 + 5 wt% Al_2O_3-doped Si_3N_4 and copper could be achieved after oxidizing the surface of Si_3N_4 at high temperature.

In this study, the direct bonding between 5 wt% MgO-doped Si_3N_4 and copper was investigated. An optimum surface oxidation condition for bonding was sought, and bonding strength variation with oxidation condition was measured. The bonding mechanism was considered also.

2. Experimental procedure

Disc type Si_3N_4 ceramics having 98% of their theoretical density was obtained by sintering Si_3N_4 powder with 5 wt% MgO addition at 1700° C for 30 min in a nitrogen atmosphere. Sintered Si_3N_4 was oxidized to prepare a metal bondable surface layer. Before oxidation, the ceramic surface was polished with a sequence of no. 200, no. 400, no. 800, and no. 1200 SiC paper. Oxidation was performed in the temperature range between 1000 and 1400° C. The oxidized surface was cleaned with acetone prior to bonding experiment.

For bonding, electrolytic copper was cut to a 7 mm × 7 mm × 7 mm cube, and the surface was prepared by polishing and cleaning following the same method as used for ceramics.

Bonding was done in a siliconit heating element furnace at 1075° C for 30 min. For the exact temperature control, a K-type thermocouple was set at the hot zone (Fig. 1). Nitrogen gas was used to maintain bonding atmosphere which contained slight oxygen.

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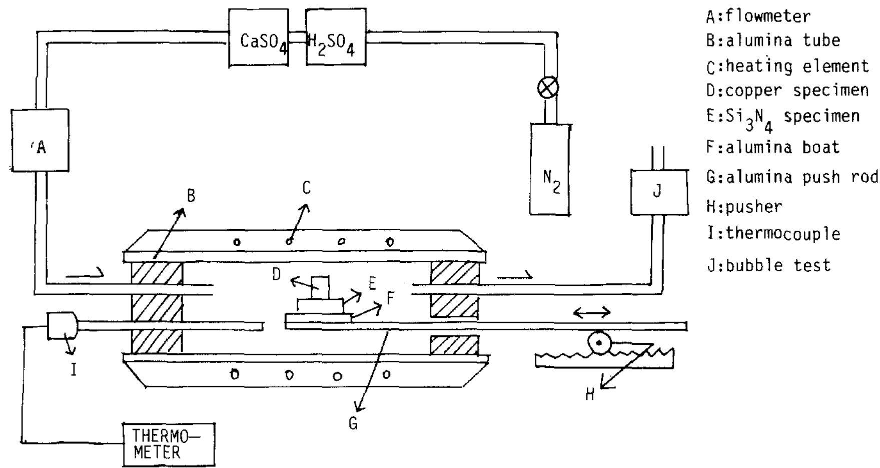


Figure 1 Experimental apparatus for bonding.

Heating and cooling of the specimen during the bonding experiment was done by a driving alumina push rod on which metal and ceramics were put together.

Bonding strength was measured by tensile test with a universal testing machine (Instron, no. 1127).

The oxide layer of Si_3N_4 ceramics and the metal–ceramic interface were examined with an X-ray diffractometer (Rigaku Inc., Japan), optical microscope (Zeiss, West Germany) and a scanning electron microscope (ETEC Autoscan, Co., Hayward, California, USA).

3. Results and discussion

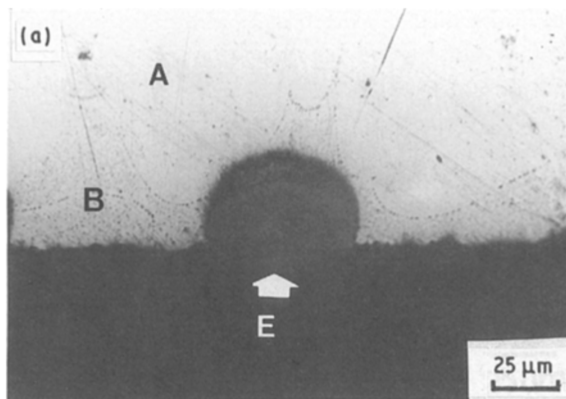
3.1. Microstructural changes of the metal–ceramic interface with oxidation temperature

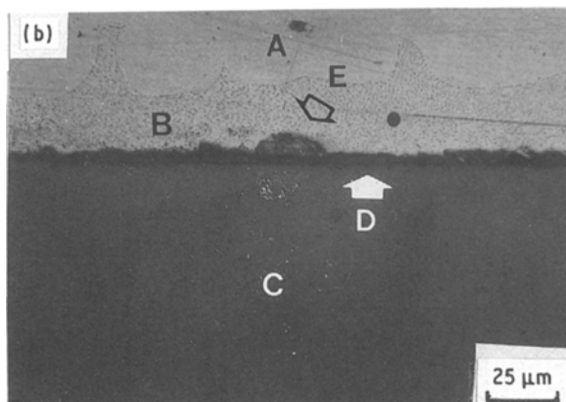
Bonding between non-oxidized Si_3N_4 ceramics and copper was attempted by DB. But bond was not achieved.

Figure 2a shows the vertical microstructure of unbonded copper. In the figure, A is the copper matrix, B is $Cu-Cu_2O$ eutectic melt formed at the bonding temperature, and E is a large pore; these large pores were formed only at the copper surface contacted to Si_3N_4. When region B was viewed in high magnification, Cu_2O precipitates about $2\,\mu m$ size could be seen at the grain boundaries of copper (Fig. 3), which confirmed the formation of $Cu-Cu_2O$ eutectic melt.

From the existence of the eutectic melt at the surface of copper, the temperature and oxygen partial pressure were assured to be the proper conditions for DB. As reported by Wittmer [17], DB between copper and ceramics can be achieved through the wetting of the ceramic surface by the $Cu-Cu_2O$ eutectic melt. So, non-oxidized Si_3N_4 seemed to be unbonded to copper by DB because the $Cu-Cu_2O$ eutectic melt does not wet the bare Si_3N_4 surface. The large pores formed at the copper surface are also considered to be related to the non-wetting of the eutectic melt.

In order to make a metal bondable surface, Si_3N_4 was oxidized at several conditions and the bondability by DB was examined. As a result, it was found that Si_3N_4 ceramics oxidized at a temperature range between 1200 and 1400° C could be bonded to copper by DB. In the case of specimens oxidized below





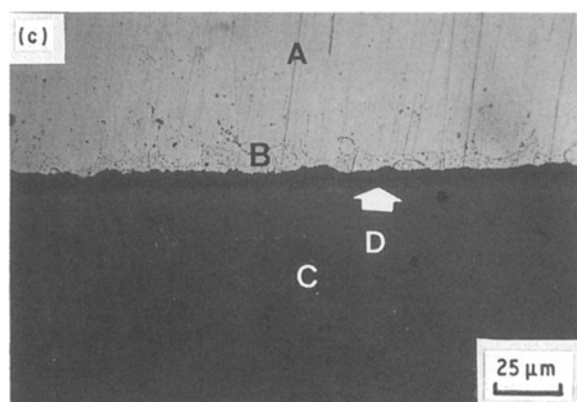


Figure 2 Optical micrographs showing (a) the vertical section of copper unbonded to non-oxidized Si_3N_4, $Cu-Si_3N_4$ interfaces of which Si_3N_4 was oxidized at (b) 1200° C, and (c) 1400° C for 1 h. ((A) copper matrix, (B) eutectic melt zone, (C) Si_3N_4 matrix, (D) oxide layer of Si_3N_4, and (E) pore).

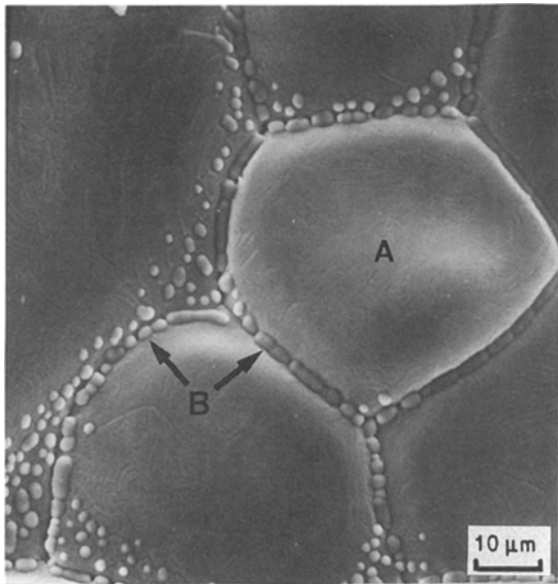


Figure 3 Scanning electron micrograph of eutectic melt zone formed at surface of copper: (A) copper grain, (B) Cu_2O precipitate.

1200° C, bonding was not achieved and the microstructure of the copper part was the same as the case of unoxidized; wetting did not occur.

Figs 2b and c are the interfacial microstructures of the bonded couple between copper and Si_3N_4 ceramics oxidized at 1200 and 1400° C for 1 h, respectively. In these figures, it could be found that bonding was achieved between the eutectic melt and the oxide layer of Si_3N_4 (marked as D in Fig. 2). The interface between the oxide layer and copper became more intimate as the oxidation temperature increased. Therefore, it was considered that the properties of the oxide layer played an important role in the bonding. So the oxide layer was analysed using an X-ray diffractometer and energy dispersive spectroscopy (EDS).

3.2. Analysis of the oxide layer

Fig. 4 shows the X-ray diffraction patterns of Si_3N_4 oxidized at 1100, 1200, 1300 and 1400° C, respectively. The oxide layer consisted of $MgSiO_3$ (clinoenstatite), Mg_2SiO_4 (forsterite), and SiO_2 (tridymite); Si_3N_4 peaks appeared at the patterns, which were considered as the matrix phase lying under the oxide layer.

From the X-ray diffraction analysis, formation of the oxide layer was inappreciable at 1100° C, but the oxide layer was apparently formed on specimens oxidized above 1200° C. As the oxidation temperature increased, the relative intensities of $MgSiO_3$ peaks increased; which means an increase of $MgSiO_3$ in the oxide layer with temperature.

Fig. 5 shows the microscopic changes of the oxide layer with oxidation temperature. At 1100° C, the surface was the same as that of the unoxidized specimen. As the temperature increased, some microscopic changes occurred; surface of the oxide layer became rough and some phases and fissures appeared. At 1400° C, the surface of the oxide layer consisted of mainly one phase (marked as A in Fig. 5d). EDS

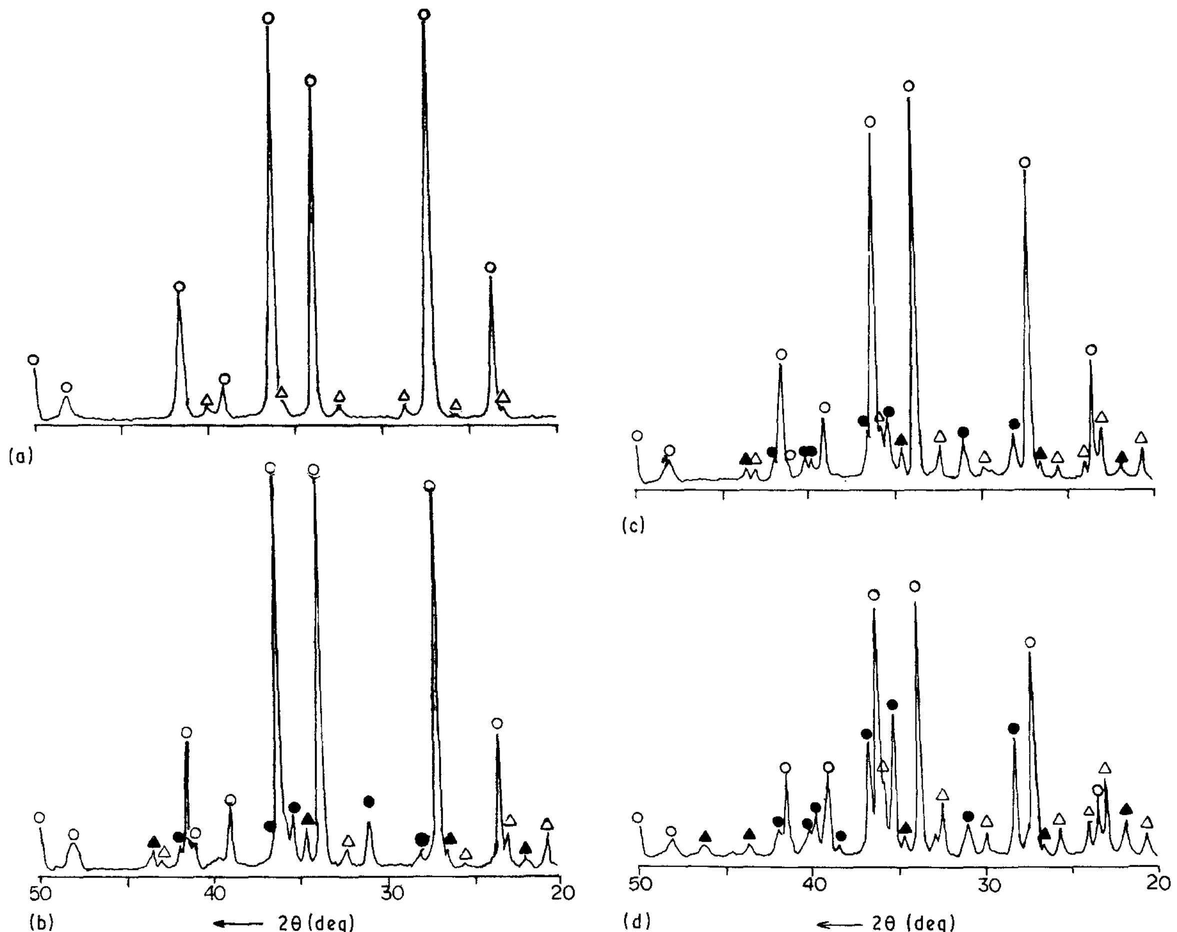


Figure 4 X-ray diffraction patterns of Si_3N_4 surface after oxidation at (a) 1100° C, (b) 1200° C, (c) 1300° C, and (d) 1400° C for 1 h. (○) β-Si_3N_4; (●) $MgSiO_3$; (△) Mg_2SiO_4; (▲) SiO_2.

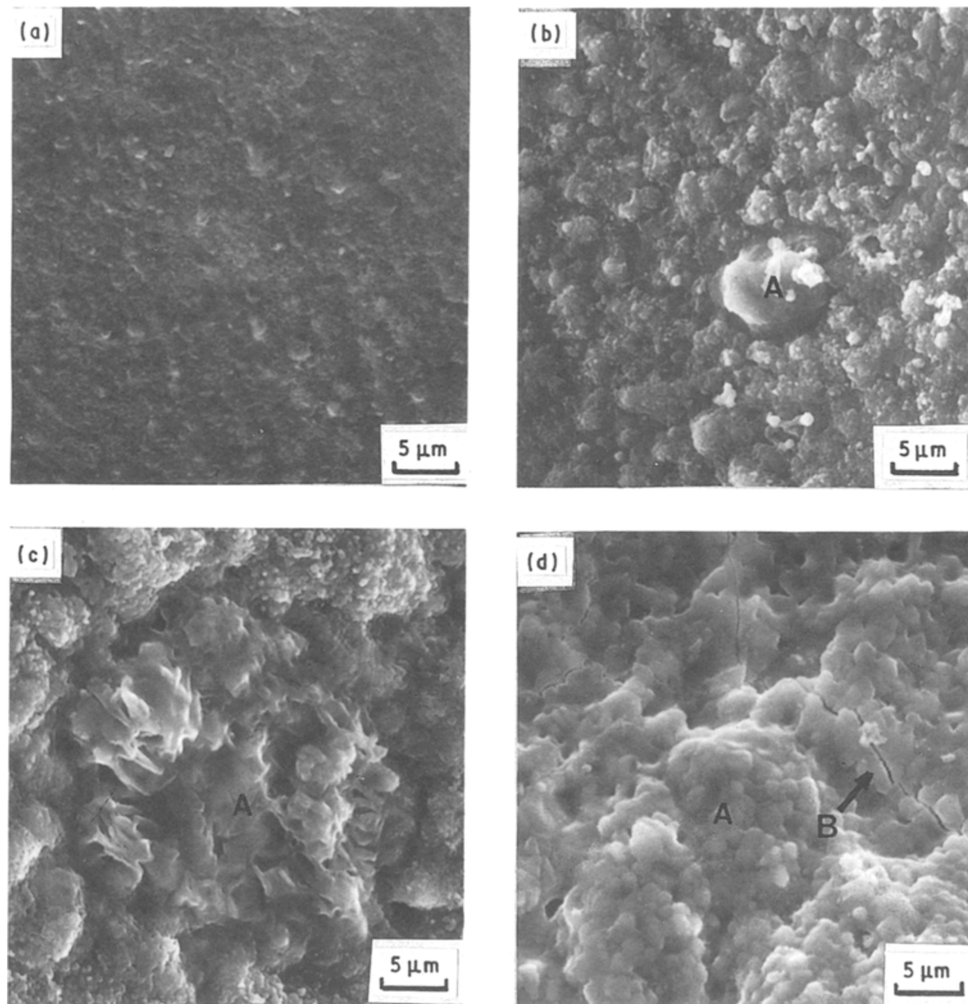


Figure 5 Scanning electron micrographs of surface of Si_3N_4 ceramics oxidized for 1 h at (a) 1100° C, (b) 1200° C, (c) 1300° C, and (d) 1400° C: ((A) $MgSiO_3$, (B) fissure).

analysis for crystal A revealed a Mg : Si atomic per cent ratio of 1. Along with X-ray diffraction analysis for the oxide layer, it was believed to be $MgSiO_3$.

From the microstructural observation of the bonded interfaces and analysis for the oxide layer, it could be noticed that as the amount of $MgSiO_3$ at the surface of the oxide layer increased, the metal–ceramic interface became more intimate. As mentioned above, wetting of Al_2O_3 by copper was enhanced by chemical reaction between Al_2O_3 and the Cu–Cu_2O eutectic melt, and the reaction product was reported as $CuAl_2O_4$ or $CuAlO_2$ [17, 19]. In this research, $MgSiO_3$ was considered to enhance the bonding, but the reaction product could not be identified in situ with the X-ray diffractometer because of the infinitesimal size of the reaction area.

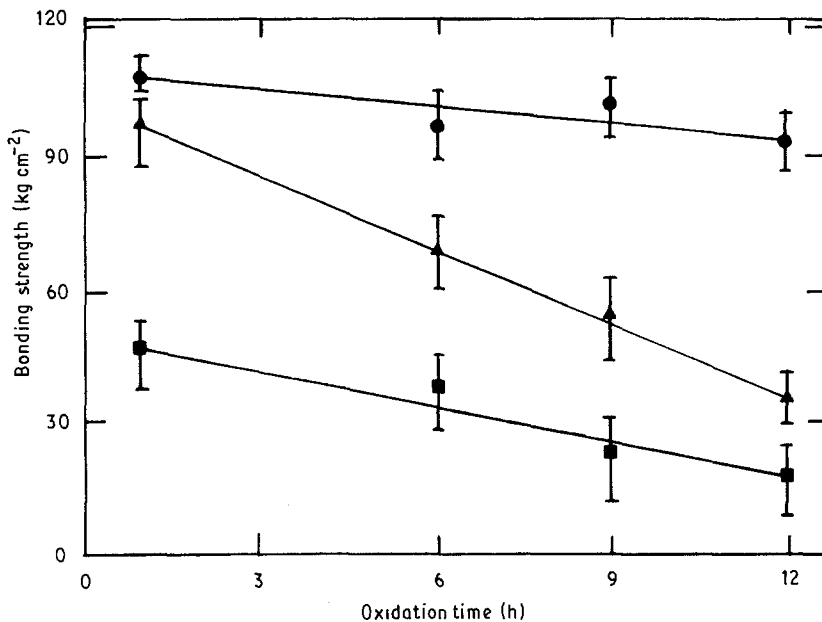


Figure 6 Plot of bonding strength variation with oxidation time and temperature; (●) 1200° C, (▲) 1300° C, and (■) 1400° C.

Tanaka *et al.* [20] reported that in the case of DB bonding between copper and Y_2O_3 + Al_2O_3-doped Si_3N_4, bonding was achieved by the reaction between the eutectic melt and glassy phase formed during oxidation of Si_3N_4. But in this study, no detectable amount of glassy phase was formed, so a different bonding mechanism seemed to act.

3.3. The effect of oxidation on the bonding strength

Fig. 6 shows the variations of room temperature bonding strength with oxidation time at 1200, 1300 and 1400° C. In all cases, debonding under tensile stress took place at the ceramic part, more strictly, at the oxide layer of the Si_3N_4 ceramics. It seemed that the bonding strength variations were related to the microstructure of oxide layer.

The microstructural and compositional change of oxide layer with oxidation temperature were observed with SEM and X-ray area scan (Fig. 7). Two remarkable phenomena were observed. One was the diffusion of magnesium ions to the surface of oxide layer; magnesium ions were added as oxide form to enhance densification of Si_3N_4. The diffusion of magnesium

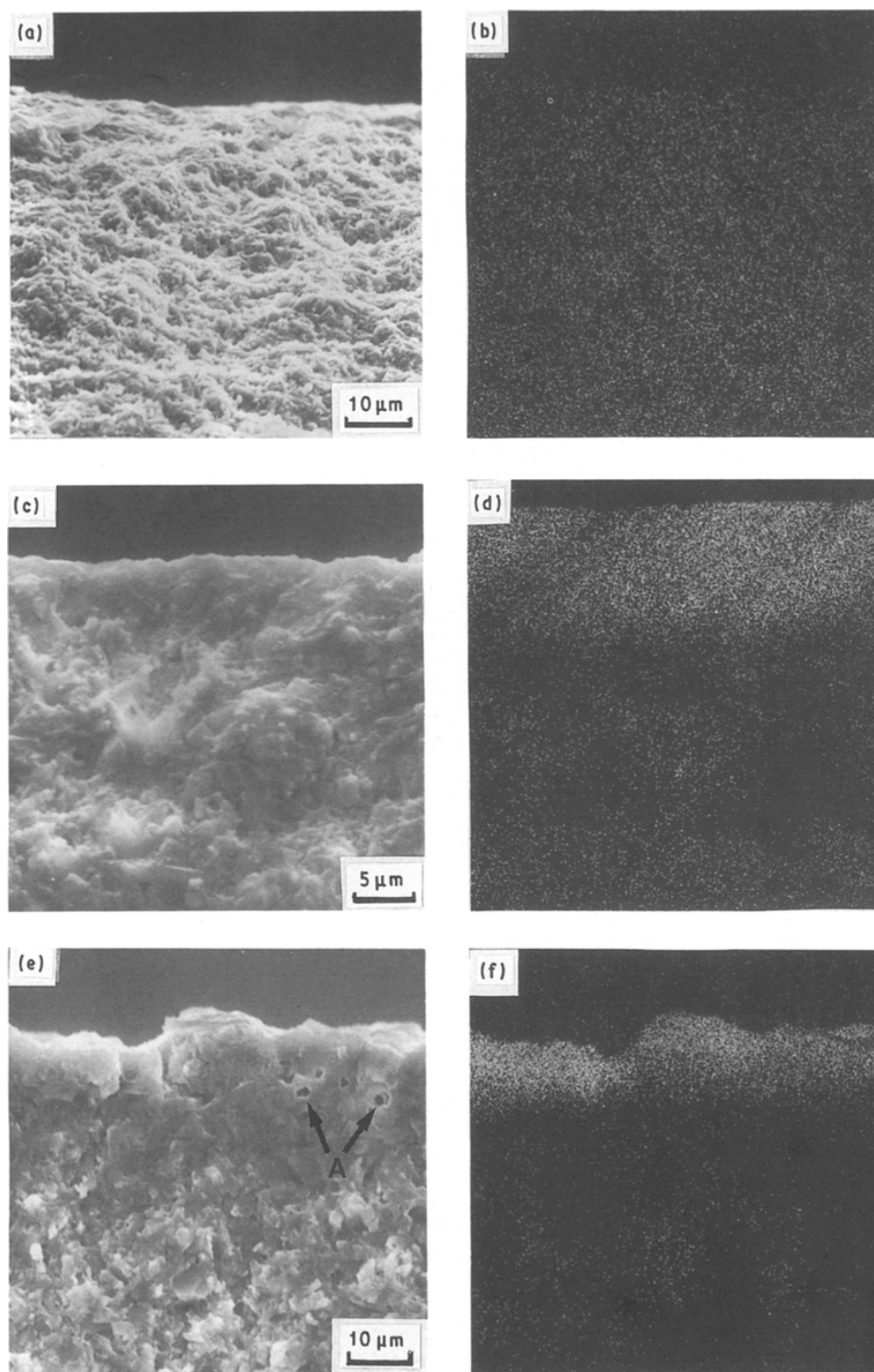


Figure 7 Scanning electron micrographs of fractured surface of oxidized Si_3N_4 ceramics and their X-ray scans for magnesium: (a), (b) at 1100° C; (c), (d) at 1200° C, (e), (f) at 1300° C, and (g), (h) at 1400° C.

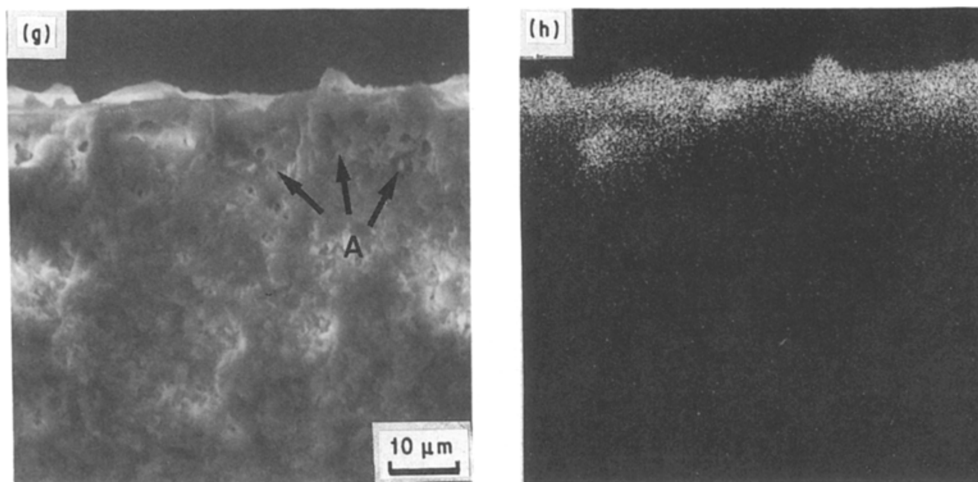


Figure 7 Continued

was activated above 1100° C and the amount of diffused magnesium increased with temperature. The diffusion and segregation of magnesium ion was consistent with the formation of $MgSiO_3$ at the surface of the oxide layer. The other phenomenon was the generation of pores in oxide layer above 1300° C. As pointed out by Tripp and Graham [22], these pores seemed to be nitrogen gas entrapped in that layer during oxidation. These pores behave as a fracture origin.

Additionally, it was also observed that the microstructure of the oxide layer remained unchanged after long exposure at 1200° C in contrast to 1300° C (Fig. 8). This seemed to be related to the slow oxidation rate at 1200° C.

So the strength variations could be explained by the microstructural effect; as oxidation temperature and time were increased, the resulting oxide layer became more porous and the bonding strength was reduced. The dense oxide layer formed at 1200° C resulted in a larger bonding strength than those of others.

4. Conclusions

Unoxidized Si_3N_4 sintered with 5 wt % MgO did not bond with copper because of the non-wetting of the Si_3N_4 surface by the Cu–Cu_2O eutectic melt formed at the copper surface. By oxidizing Si_3N_4 above 1100° C, bonding could be achieved. During oxidation, magnesium ion added as a sintering aid diffused out to the surface and formed oxidation products such as Mg_2SiO_4 and $MgSiO_3$. Among them, $MgSiO_3$ seemed to be related to the bonding; as the amount of $MgSiO_3$ increased, the metal–ceramic interface became more intimate. But the bonding strength was controlled not by the interface but by the oxide layer of Si_3N_4. As the oxidation temperature and time were increased, the oxide layer became more porous and the bonding strength was reduced.

References

1. A. GIACHELLO, P. C. MARTINENGO, G. TOMMASIMI and P. POPPER, *J. Mater. Sci.* **14** (1979) 2825.
2. G. HIMSOLT and H. KNOCH, *J. Amer. Ceram. Soc.* **62** (1, 2) (1979) 29.
3. L. J. SCHIOLER, *Amer. Ceram. Soc. Bull.* **64**(2) (1986) 268.
4. S. S. COLE and G. SOMMER, *J. Amer. Ceram. Soc.* **44**(6) (1961) 265.
5. R. M. FULRATH and E. L. HOLLER, *Amer. Ceram. Soc. Bull.* **47**(5) (1968) 493.
6. J. T. KLOMP, *ibid.* **51**(9) (1972) 683.
7. A. WICKER, PH. DARBON and F. GRIVON, in Proceedings of International Symposium on Ceramic Components for Engine, Hakone, October 1983 edited by S. Somiya, E. Kanai, and K. Ando (D. Reidel Pub. Co., Boston, 1984) p. 716.
8. H. MIZUHARA and K. MALLY, *Welding J.* **64**(10) (1985) 27.

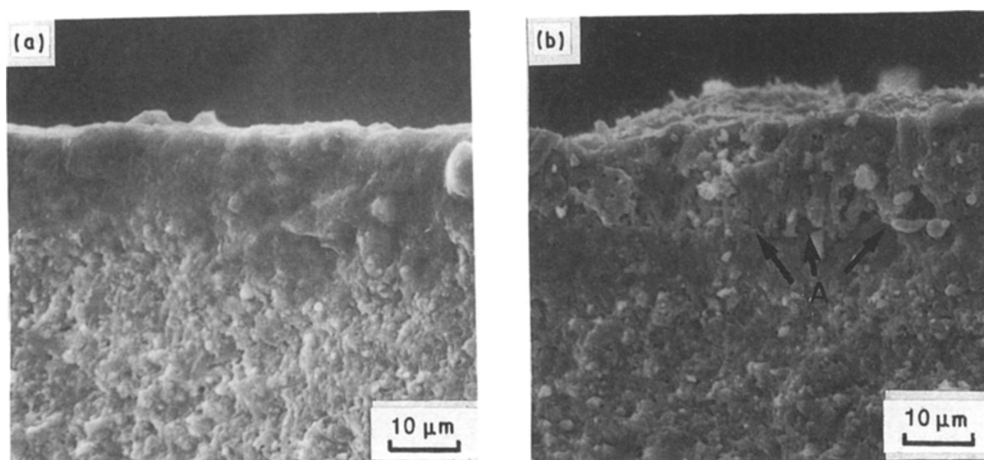


Figure 8 Scanning electron micrographs of vertical section of Si_3N_4 oxidized for 12 h at (a) 1200° C, and (b) 1300° C.

9. G. ELSSNER, W. DIEN and J. S. WALLACE, in "Engineering Applications of Ceramic Materials" edited by M. M. Schwartz (American Society for Metals, Boston, Ohio, 1985) p. 216.
10. K. SUGANUMA, M. TAKAGI, Y. MIYAMOTO, M. KOIZUMI, T. OKAMOTO and H. NAKATA, *J. Ceram. Soc. Jpn* **96**(11) (1988) 1051.
11. A. KOHNO, S. HIOKI, T. YAMADA and N. NAKAE, in "Special Ceramics" Vol. 8, edited by S. P. Howlett and D. Tayler (The Institute of Ceramics, Staffs, 1986) p. 125.
12. T. YAMADA, A. KOHNO and S. HIOKI, in "Ceramic Material and Components for Engines", edited by W. Bunk and H. Hausner (American Society for Metals, Boston, Ohio, 1986) p. 401.
13. M. J. RAMSEY and M. H. LEWIS, *Mat. Sci. Eng.* **71** (1985) 113.
14. J. E. SIEBELS, in "Progress in Nitrogen Ceramics", edited by F. L. Riley, (Nijhoff Pub. Co., Hague, 1983) p. 455.
15. F. BURGESS, US Patent 3 766 634 (1973).
16. Y. S. SUN and J. C. DRISCOLL, *IEEE Trans. on Electron Devices*, Ed-23(8) (1976) 961–67.
17. M. WITTMER, in "Electron Packaging Material Science", edited by E. A. Giess, K. N. Tu and D. R. Uhlmann, (Material Research Society, Pennsylvania, 1985) p. 393.
18. D. K. KIM, MSc Thesis, Korea Advanced Institute of Science and Technology (1984).
19. W. LISHI, J. HAAG and G. PETZOW, in "Microstructure and Properties of Ceramic Materials", edited by T. S. Yen and J. A. Pask, (Science Press, Beijing, China, 1984) p. 125.
20. P. K. WEISS and J. GOBRECHT, in "Electron Packaging Material Science", edited by E. A. Giess, K. N. Tu and D. R. Uhlmann, (Material Research Society, 1985) pp. 399–404.
21. S. I. TANAKA, K. NISHIDA and T. OCHIAI, in Proceedings of International Symposium on Ceramic Components for Engine, Hakone, October 1983 edited by S. Somiya, E. Kanai, and K. Ando (D. Reidel Pub. Co., 1984) pp. 249–56.
22. W. C. TRIPP and H. C. GRAHAM, *J. Amer. Ceram. Soc.* **59**(9–10) (1976) 399.

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