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# Silver–Alumina Solid State Bonding: Study of Diffusion and Toughness Close to the Interface

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## Abstract

*The study of Ag/$Al_2O_3$ interfaces achieved by solid state bonding shows that silver diffuses in alumina during the joining process and later annealings. This diffusion, particularly along grain boundaries, is correlated to the decrease of the toughness of alumina observed at the same time close to the metal–ceramic interface.*

*Die Untersuchung von Ag/$Al_2O_3$-Grenzflächen, hergestellt durch Festkörperverschweißung, zeigt, daß Silber während des Verschweißens und des anschließenden Anlassens in das Aluminiumoxid diffundiert. Es besteht eine Korrelation zwischen der Diffusion des Silbers, besonders entlang der Korngrenzen, und der Abnahme der Zähigkeit des Aluminiumoxids in der Nähe der Metall–Keramik-Grenzfläche.*

*L'étude d'interfaces réalisées par liaison à l'état solide montre que l'argent diffuse dans l'alumine au cours de l'élaboration et de recuits ultérieurs. Cette diffusion, en particulier le long des joints de grains, est corrélée à la chute de ténacité de l'alumine observée en parrallèle près de l'interface métal-céramique.*

## 1 Introduction

The fracture of a metal–ceramic bond can be adhesive (interfacial) or cohesive in the bulk. In the latter case, it usually occurs in the ceramic, but often for strengths markedly lower than the fracture strength of the ceramic alone.[1] The common noticeable difference between the coefficient of thermal expansion of the materials to be joined, resulting in residual stresses, is one of the factors that explains this phenomenon.[2–4] Nevertheless another rarely studied parameter can be put forward, i.e. the diffusion of atoms or ions into the ceramic.

For this study, the easy case of the silver–alumina system, obtained by a solid state bonding process,[5] has been selected. The two aims will be:

- the study of the silver diffusion in alumina during the joining or later annealings
- the study of the toughness of alumina near the interface for bonding conditions leading to cohesive fractures in alumina.

## 2 Materials and Methods

For this study, 99·9% pure single crystals of alumina (sapphire, Criceram Rubis) and technical 99% alumina (SCT, Société des Céramiques Techniques) which presents a fine microstructure with an average grain size of about 5 $\mu$m have been used. The sapphire samples were diamond polished leading to an average surface roughness $R_a = 0{\cdot}008\,\mu$m and technical alumina was bonded as sintered ($R_a = 0{\cdot}25\,\mu$m). The silver (99·9%) used in this study was either annealed in air at 900°C for one week (designated Ag–O, total oxygen content from chemical analysis: 620 ppm) or cold rolled (rolling reduction 90%, oxygen content: 160 ppm).

The specimens were obtained by solid state bonding[6,7] in air. The samples are shown schematically in Fig. 1, and are made up of two alumina cylinders (12 mm and 8 mm diameter and 3 mm

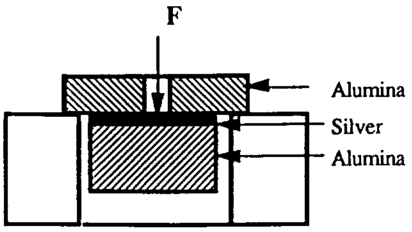

**Fig. 1.** Push test sample.

thick) joined by a silver foil (0·25 mm thick). This sample allows an indirect tensile test (push text) to be performed, which characterizes the mechanical resistance of the bond. During testing, the load is applied on the silver part by means of a cylinder (Fig. 1).

## 3 Silver Diffusion during Solid State Bonding

Diffusion of silver in sapphire was studied by SIMS.[8] Samples was elaborated by solid state bonding for 2 h at 900°C under 6 MPa, then annealed in air for 8 h. Before bonding, some sapphire samples were annealed at 1500°C, others were kept as polished. Silver was removed by chemical etching before SIMS analysis.

Figure 2(a) and (b) show the silver penetration profile in sapphire annealed at 1500°C (after polishing, before bonding) and untreated after polishing, in logarithmic and in gausso-arithmetic coordinates, respectively. They confirm the effect of the polishing on the silver diffusion described by Badrour and coworkers.[9–11] The common part to the curves corresponds to the diffusion in the bulk. The influence of the dislocations due to the mechanical polishing,[9] and consequently present in non-annealed alumina, leads in this case to a second part of the curves that may be interpreted by the diffusion of silver along dislocations. The bulk diffusion coefficient of silver (deduced from the first part of the curve) is equal to $D_v = 4 \times 10^{-21}\,\mathrm{m^2\,s^{-1}}$. This value is close to those obtained at the same temperature from thin deposited silver films on single crystals of alumina as reported by Moya *et al.*[12] and shown in Fig. 3. It can be concluded that the metal diffusion into the ceramic is effective during solid state bonding and the diffusion kinetics are close to those observed during infinite dilution diffusion from thin deposits.

Under these conditions, the bulk average penetration of silver in alumina during solid state bonding may be estimated from $(D_v t)^{1/2}$ ($t$ = diffusion time). It is equal to $5 \times 10^{-3}\,\mu$m for 2 h, 0·01 $\mu$m for 6 h and 0·05 $\mu$m for 192 h. To investigate the effect of this diffusion on the mechanical resistance of the bond, polycrystalline push test samples (Fig. 1) were prepared for 4 h in air under 6 MPa at 900°C. After bonding these samples were annealed in air at the same temperature for different times. Figure 4 shows the variation of the tensile fracture strength of the bonded samples versus annealing time; a small decrease of the mechanical resistance is observed. Whatever the time, the fracture always occurs in

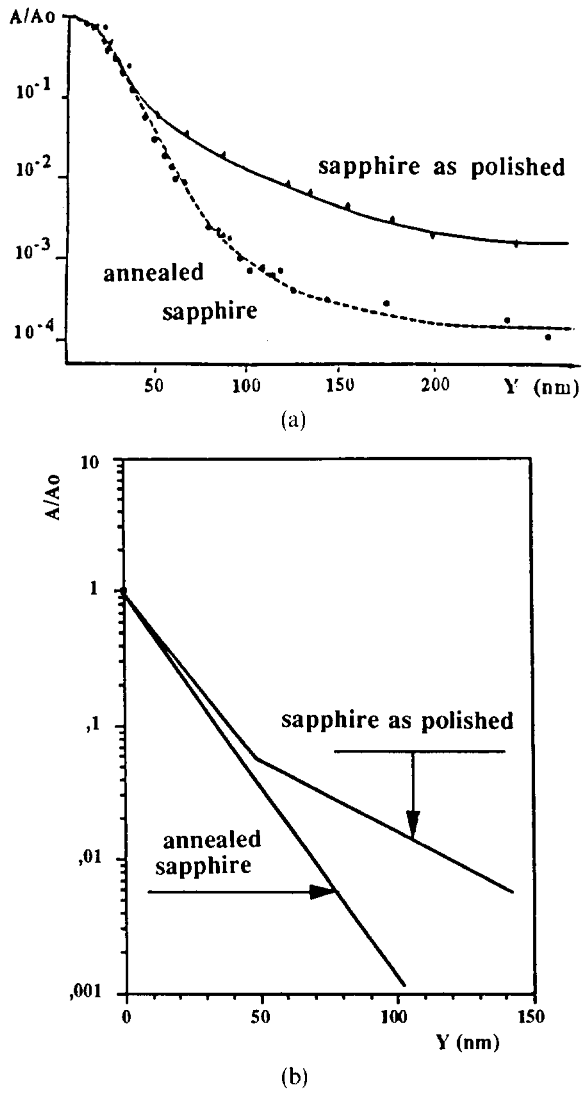

**Fig. 2.** Silver diffusion profile in sapphire, after solid state bonding and annealing, (a) logarithmic coordinates, and (b) gausso arithmetic coordinates.

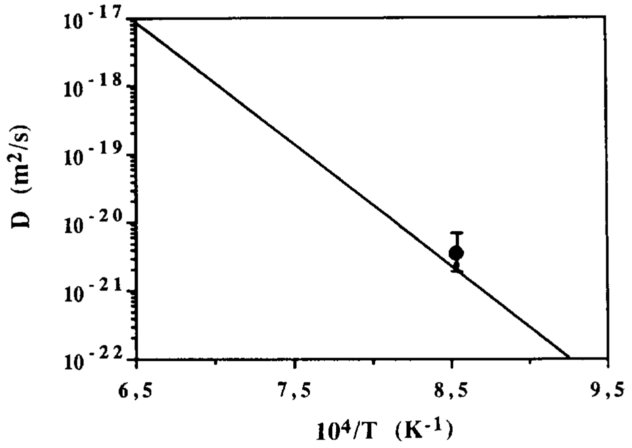

**Fig. 3.** Bulk silver diffusion coefficient in sapphire versus temperatures;[12] (——), infinite dilution diffusion;[12] (●), this study.

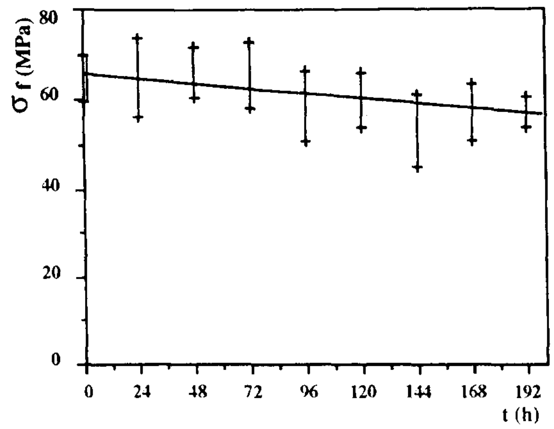

**Fig. 4.** Tensile fracture stress of Ag–O/$Al_2O_3$ samples versus annealing time at 900°C in air.

alumina (cohesive fracture), in a zone which moves further away from the interface with longer annealing times.

These results show that a correlation exists between the alumina embrittledness near the interface and the annealing time, and thus the silver diffusion. To confirm this point, the mechanical behaviour of the ceramic close to the metal–ceramic interface was more precisely studied.

## 4 Influence of Solid State Bonding and Diffusion Annealings of the Alumina Toughness

Push test samples were cut perpendicularly to the interface, then polished and annealed at 900°C for different times. Two solid state bonding conditions were selected:

—The first one corresponds to classical conditions ($P = 6$ MPa; $t = 4$ h; $T = 900$°C) using an annealed silver joint saturated with oxygen. As has been shown[13,14] the presence of oxygen is favourable to the bond resistance.

—The second one corresponds to $P = 3$ MPa; $t = 0$ h; $T = 900$°C with a highly cold rolled (90%) silver joint. A previous study[5] showed that cold rolling could accelerate the adhesion processes, since optimal bonding is obtained without any plateau at 900°C.

In both cases, fractures are cohesive in alumina. The tensile fracture strengths obtained are 70 MPa and 75 MPa, respectively. Vickers indentations (applied load 3 N) in alumina were made, every 50 μm, from the Ag/$Al_2O_3$ interface (depth 0) to the ceramic bulk. The fracture toughness was calculated from the Liang *et al.* formula:[15]

$$K_{IC} = (H_v a^{1/2}/\alpha)(E\Phi/H_v)^{0\cdot4}(c/a)^{c/(18a-1\cdot51)}$$

where $H_v$ = Vickers' hardness; $E$ = Young's modulus (320 GPa for alumina); $\Phi$ = constraint factor ( = 3 for

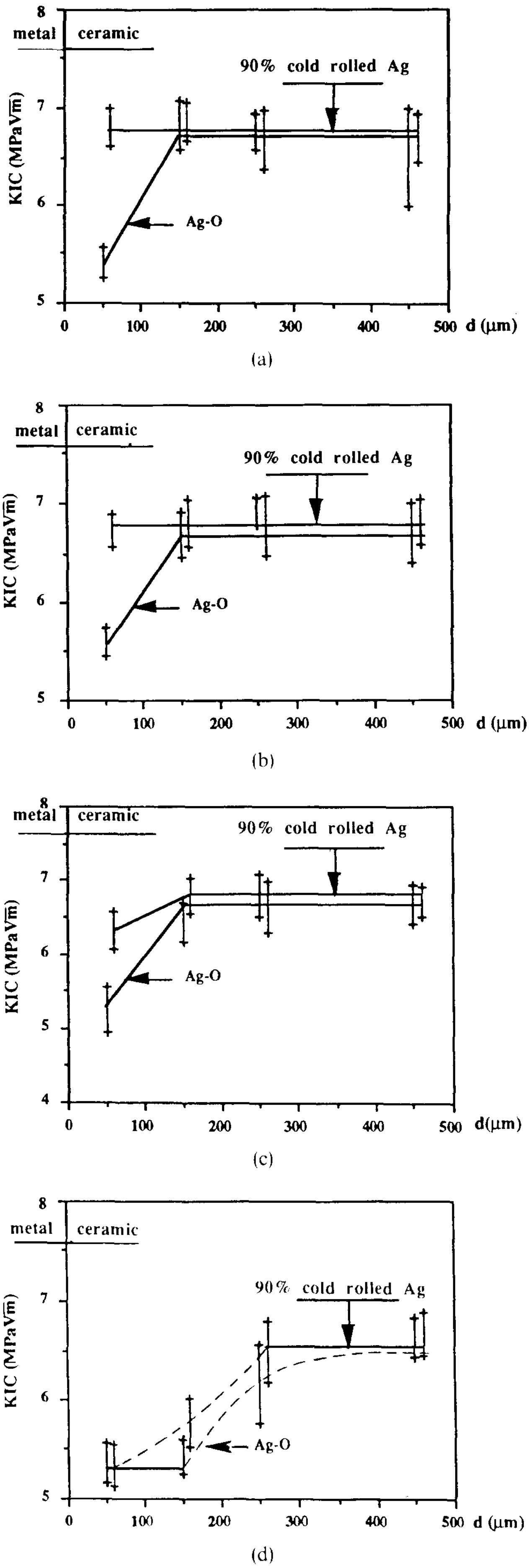

**Fig. 5.** Fracture toughness of alumina versus distance from the silver–alumina interface; (a) as elaborated; (b) after 72 h annealing at 900°C; (c) after 96 h at 900°C; (d) after 192 h annealing at 900°C.

alumina); and $\alpha$ = non-dimensional constant function of the Poisson's ratio $\nu$, given by:

$$\alpha = 14[1 - 8(4\nu - 0{\cdot}5)^4/(1+\nu)^4]$$

and where $c$ is the crack radius and $a$ the diagonal length of the indent.

The results, obtained for different annealing times, are reported in Fig. 5. They show a decrease of $K_{\mathrm{IC}}$ close to the interface which is reduced as much as the time of annealing at 900°C is increased. For Al$_2$O$_3$/Ag–O joints, the $K_{\mathrm{IC}}$ value is equal to 5·5 MPa$\sqrt{\mathrm{m}}$ at 50 $\mu$m from the interface. The decrease is observed immediately after bonding and is not drastically influenced by further annealing up to 120 h. After 192 h, decrease of $K_{\mathrm{IC}}$ is still measurable at 250 $\mu$m from the interface. On the other hand, no change is observed for Al$_2$O$_3$/cold rolled Ag couples after bonding and after annealing up to 72 h (Fig. 5(b)). After that time, the $K_{\mathrm{IC}}$ of alumina bonded to cold rolled silver begins to decrease to reach 6·2 MPa$\sqrt{\mathrm{m}}$ at a depth of about 50 $\mu$m (Fig. 5(c)). The embrittled depth increases with the annealing time and it is higher than 150 $\mu$m after 192 h (Fig. 5(d)).

Figure 6 shows the variation of $K_{\mathrm{IC}}$ versus annealing time at a depth of 50 $\mu$m: the toughnesses of the two systems are only equal after 192 h.

To complete these results, indentations were made on an alumina surface which was previously bonded to silver (silver was chemically removed). The measurements were performed in two areas: the area initially bonded to silver (b area) and the one outside (a area), as shown in Fig. 7. The results are plotted in Fig. 8 and confirm the previous observations: for the Ag–O/Al$_2$O$_3$ system, marked decrease of $K_{\mathrm{IC}}$ is observed in the b area initially bonded to silver, from 6·5 MPa$\sqrt{\mathrm{m}}$ average value (a area) to 5·5 MPa$\sqrt{\mathrm{m}}$ (b area) (Fig. 8(a)). The same behaviour was observed whatever the annealing time.

In the case of Al$_2$O$_3$/cold rolled Ag couple, no significant difference was noted in the fracture toughness in the two regions (a and b) for short

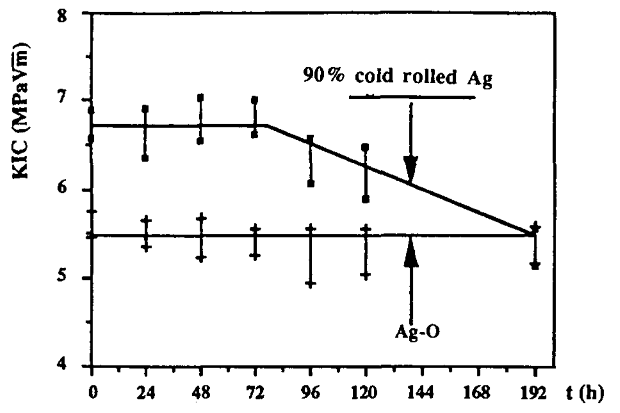

**Fig. 6.** Fracture toughness variation of alumina at 50 $\mu$m from the interface.

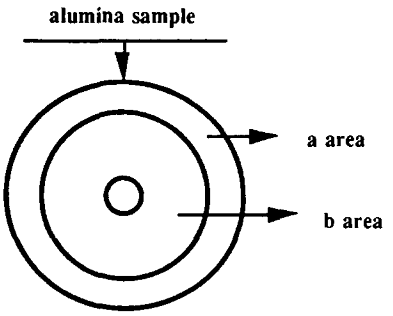

**Fig. 7.** Alumina push-test sample; a area, silverless; b area, initially bonded to silver.

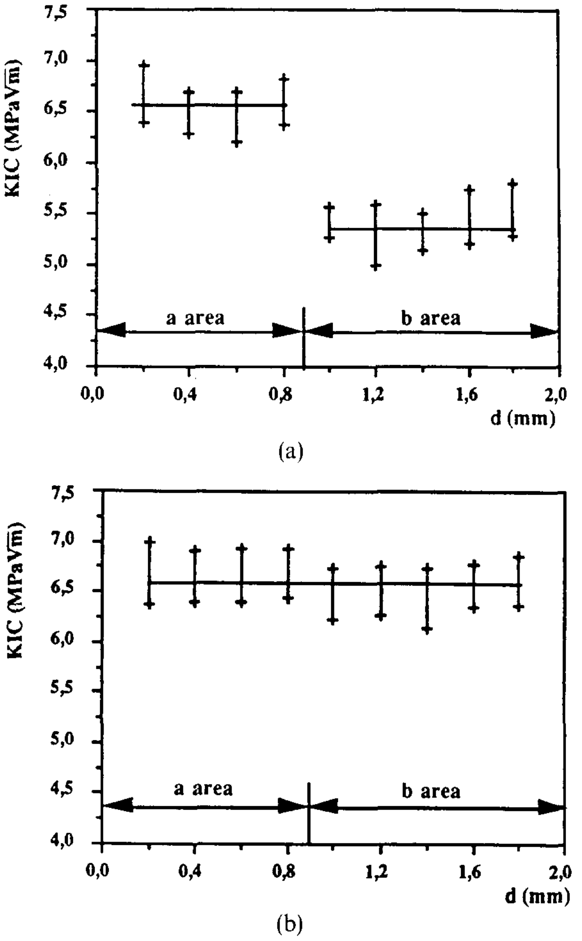

**Fig. 8.** Fracture toughness of alumina across a and b areas: (a) Ag–O/Al$_2$O$^3$ system as bonded; (b) cold-rolled Ag/Al$_2$O$_3$ as bonded.

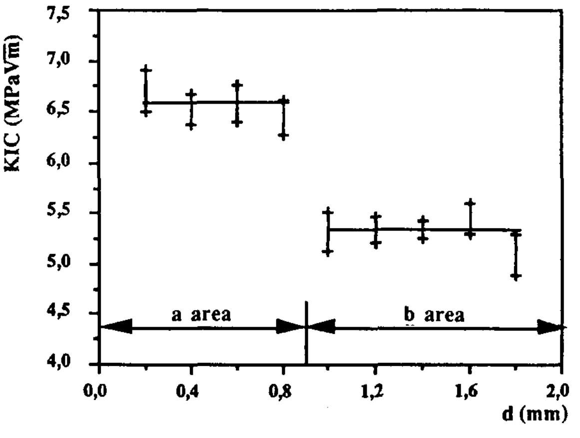

**Fig. 9.** Fracture toughness of alumina across a and b areas of cold-rolled Ag/Al$_2$O$_3$ system annealed 192 h at 192°C.

annealing times (Fig. 8(b)). However, after 192 h at 900°C, this difference becomes sizeable: $K_{IC}$ decreased from 6·5 MPa$\sqrt{m}$ average value to 5·3 MPa$\sqrt{m}$, as shown in Fig. 9.

## 5 Discussion

These results confirm that the polycrystalline alumina toughness is modified by solid state bonding and by diffusion annealing. This effect is more pronounced for an annealed joint (Ag–O 4 h solid state bonded at 900°C) than for a cold rolled joint (Ag, 0 h at 900°C). However, the time difference cannot totally explain these results, since with a cold rolled joint, the fracture toughness (at 50 $\mu$m from the interface) only decreases after 72 h annealing. So, it seems that the embrittlement of alumina is more pronounced under load (during solid state bonding) than for pressureless annealing. This may be explained by the concept of the space charge physics[16,17] showing that in an insulator submitted to mechanical stresses, charges are trapped on 'sites' (lattice distorsions, impurities, grain boundaries, dislocations, etc.) where the polarizability of the medium is modified, forming a space charge. The field of the trapped charges twists the lattice, which gains locally an energy of polarization. Preliminary calculations show that an energy of 5 eV or more per trapped charge would be available.[17] The relaxation of this energy can lead to the fracture of the ceramic. Consequently, the toughness of an insulator depends on the trapping sites present in material.

During solid state bonding two mechanisms can create trapping sites:

—the friction between metallic joint and ceramic;[18,19]

—the diffusion of silver into alumina.[19]

Therefore, solid state bonding can induce a decrease of the ceramic properties. However, the diffusion studies achieved with single crystals indicate that the depths affected by silver penetration in the bulk are about 0·01 $\mu$m for 6 h and 0·05 $\mu$m for 192 h, thus much lower than those corresponding to the fall of the toughness (> 150 $\mu$m for 192 h). This difference may be due to the important contribution of grain boundary diffusion in polycrystalline alumina shown by Badrour *et al.*[11] To confirm this point sapphire previously bonded to silver has been indented ($P = 6$ MPa, $t = 4$ h, $T = 900$°C for Ag–O/sapphire couple and $P = 3$ MPa, $t = 0$ h, $T = 900$°C for cold rolled Ag/sapphire couple). Toughness was measured in the two areas a and b described previously. The $K_{IC}$ of sapphire is plotted in Fig. 10(a) and (b), for a non-annealed sample and for a sample annealed 192 h at 900°C, respectively. No variation of $K_{IC}$ in the two areas a and b was observed, whatever the initial preparation of silver and annealing time. The comparison of these results with ones obtained using polycrystalline alumina (Figs 8 and 9) seems to indicate that grain boundary diffusion has a dominant role in controlling ceramic embrittlement. Indeed, from the measurements of Badrour *et al.*[11] it was observed that silver penetrated deeper in polycrystalline alumina than in single crystals, 300 $\mu$m and 20 $\mu$m at 916°C for 240 h, respectively, whereas 300 $\mu$m corresponds approximately to the depth where toughness is reduced for equivalent treatments.

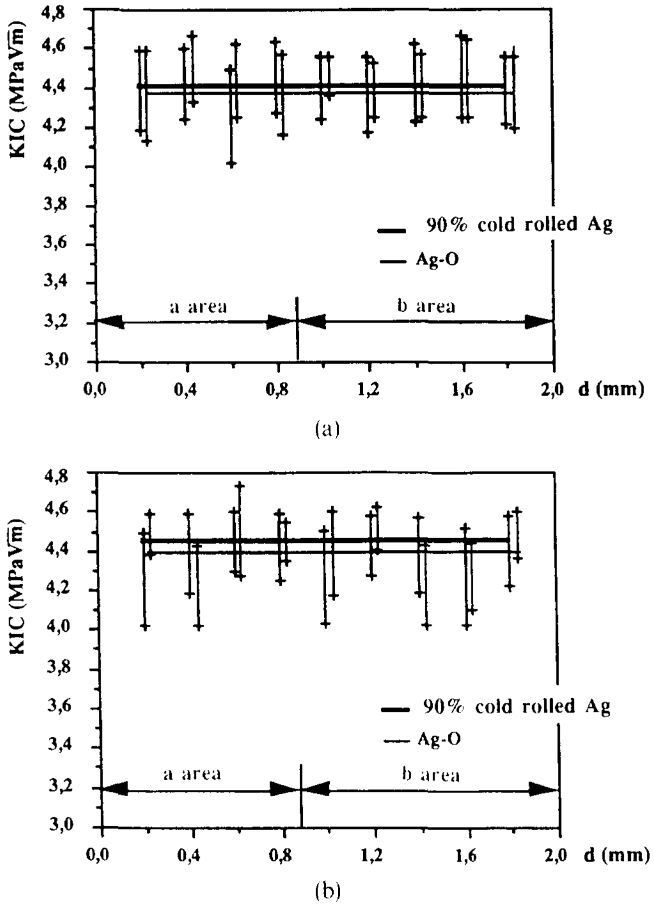

**Fig. 10.** Fracture toughness of sapphire across a and b areas; (a) Ag/sapphire system as bonded; (b) Ag/sapphire system annealed 192 h at 900°C.

This embrittlement of alumina during diffusion can have different causes:

(i) Chemical effect:
Silver segregation can occur on grain boundaries and intergranular films (MgO, $SiO_2$, $MgAl_2O_4$) present in technical alumina can be modified. The result of this is changes in volume which generates stresses in grain boundaries and bulk. This embrittlement due to grain boundary diffusion is currently observed in oxidation mechanisms.[20]

(ii) Size effect:
Silver atoms or ions ($Ag^0$ or $Ag^+$) are large compared to Al ions. Therefore silver diffu-

sion can lead to distortions of lattice and then to stresses.

(iii) Electrostatic effect:
The aluminium vacancies are negatively charged ($3^-$) compared with the lattice. So they create a repulsive interaction with $Ag^0$ or $Ag^+$ on a $Al^{3+}$ site. This repulsion can lead to a lattice distortion generating the internal stresses favouring toughness decrease.

In other words, silver diffusion corresponds to the forming, in the bulk and in grain boundaries, of various trapping sites of charges. Under stresses of any kind (electrical, mechanical, etc.) a space charge can be formed in the ceramic. Polarization energy is stored, leading to a decrease in toughness due to the relaxation of this energy in bulk or along grain boundaries as shown by Le Gressus and coworkers.[17,21]

## 6 Conclusion

The role of the diffusion of metal into the ceramic during non-reactive solid state bonding has never been studied previously. The authors have shown that during the bonding itself and during annealing, silver diffuses into the bulk, along the grain boundaries and the dislocations of the ceramic. The kinetics, measured by SIMS, are identical to those observed during infinite dilution diffusion. This diffusion seems to play a major role in controlling the mechanical properties of alumina near the junction, but, on the other hand, it has no influence on the thermodynamical adhesion, since excellent bonds were observed for short times with cold-rolled silver.

In the same way, the authors have measured by indentation a significant decrease of the toughness of polycrystalline alumina near the silver–ceramic interface. It decreases from 6·5 MPa$\sqrt{m}$ in the bulk to about 5·3 MPa$\sqrt{m}$ near the interface. The volume concerned increases with the annealing time, which suggests that this embrittlement is not only due to the residual stresses in the ceramic induced by the difference in the coefficients of thermal expansion between silver and alumina, but also to the silver diffusion. Moreover it seems that grain boundary diffusion is a cause of this effect which only appears in polycrystals.

## Acknowledgement

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## References

1. Allen, R. V. & Borbidge, W. E., Solid state metal bonding of platinum to alumina. *J. Mater. Sci.*, **18** (1983) 2835–43.
2. Evans, A. G. & Hsueh, C. H., Residual stresses in metal/ceramic bonded strips. *J. Amer. Ceram. Soc.*, **68**(5) (1985) 241–8.
3. Schmidt-Brücken, H. & Schlapp, W., Ein neues Verfahren zur Metal/Keramik-Verbindung. *Keram. Z.*, **23**(5) (1971) 278–80.
4. Suganuma, K., Okamoto, T., Koizumi, M. & Shmida, M., Joining of silicon nitride to silicon nitride and to Invar alloy using an aluminium interlayer. *J. Mater. Sci.*, **22** (1987) 1359–64.
5. Sérier, B. & Tréheux, D., Silver–alumina solid state bonding: influence of the work hardening of the metal. *Acta Metall. Mater.*, **41**(2) (1993) 369–74.
6. Courbière, M., Etude des liaisons céramique-métal: application au couple cuivre–alumine. Thèse de l'Ecole Centrale de Lyon, October 1986.
7. Courbière, M., Tréheux, D., Béraud, C. & Esnouf, C., Liaisons métal–céramique: techniques et aspects physico-chimiques. *Ann. Chim. Fr.*, **12** (1987) 295–312.
8. Moya, F., Moya, E., Juvé, D., Tréheux, D., Grattepain, C. & Aucouturier, M., SIMS study of copper diffusion into bulk alumina. *Scripta Metall. Mater.*, **28**(3) (1993) 343–8.
9. Badrour, L., Diffusion volumique et intergranulaire de l'argent dans l'alumine alpha. Thèse de l'Université de Droit, d'Economie et des Sciences d'Aix-Marseille, March 1986.
10. Badrour, L., Moya, E. G., Bernardini, J. & Moya, F., Bulk diffusion of $^{110}Ag$ tracer in $Al_2O_3$. *Scripta Metall.*, **20** (1986) 1217–22.
11. Badrour, L., Moya, E. G., Bernardini, J. & Moya, F., Fast diffusion of silver in single and polycrystals of α-alumina. *J. Phys. Chem. Solids*, **50**(6) (1989) 551–61.
12. Moya F., Juvé, D. & Tréheux, D., SIMS study of silver diffusion into bulk alumina. (To be published).
13. Sérier, B., Etude et charactérisation des liaisons céramique–métal élaborées par thermocompression: application au couple argent–alumine. Thèse de l'Ecole Centrale de Lyon, July 1991.
14. Tréheux, D. & Juvé, D., Damage of ceramic–metal interface In *Mechanics and Mechanisms of Damage in Composites and Multimaterials*, ed. D. Baptiste. Mechanical Engineering Publications, London, 1991, pp. 361–75.
15. Liang, K. H., Orange, G. & Fantozzi, G., Evaluation by indentation of fracture toughness of ceramic material. *J. Mater. Sci.*, **25** (1990) 207–14.
16. Blaise, G., Microscopic and macroscopic description of the polarization of dielectric materials. The concept of polaron applied to the conduction and trapping of charges. *Le Vide, les couches Minces-Supplément*, **260** (1992) 1–27.
17. Blaise, G. & Le Gressus, C., Flashover in insulators related to the destabilization of a localized space charge. *C.R. Acad. Sci. Paris*, **314** (1992) 1017–24.
18. Fayeulle, S., Berroug, A., Hamzaoui, B., Treheux, D. & Le Gressus, C., Role of dielectric properties in the tribological behaviour of insulators. *Wear*, **162–164** (1993) 906–12.
19. Berroug, A., Fayelle, S., Hamzaoui, B., Tréheux, D. & Le Gressus, C., Effect of X-irradiation and friction on the properties of Insulators. *IEEE Trans. on Electrical Insulation*, **28**(4) (1993) 528–34.
20. Beranger, G. & Coddet, C., Oxydation des métaux à haute température. Rôle des contraintes internes. *J. Microscop. spectroscope. électroniques*, **5** (1980) 793–814.
21. Le Gressus, C., Gautier, M. & Duraud, J. P., Propriétés de surface et propriétés techniques des céramiques. Fracture mécanique et claquage diélectrique. *Revue Scientifique et technique de la défense*, 2ème trimestre (1990) 67–82.