Ceramics International **21** (1995) 395–398

Interface Strengths in a ZrO_2/Ag–Cu–Al–Ti System

Youngmin Lee[a] & Jin Yu[b]

[a]PKG Development, Samsung Electronics Co., Ltd, Seoul, Korea
[b]Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology PO Box 201, Chongryang, Seoul, South Korea

(Received 11 November 1994; accepted 28 January 1995)

Abstract: Interface strengths of ceramic/metal joints were investigated using the brazed ZrO_2/Ag–Cu–Al–Ti joints prepared under various processing conditions. Interface microstructures and chemistries were investigated using optical microscopy, SEM, X-ray, AES and correlated with flexural strength measurements obtained from the four point bend tests. The amount of segregated S and the thickness of brittle TiO/Al_2O_3 layers at the interface were found to be the major factors affecting the interface strength.

1 INTRODUCTION

Brazing of ceramic and metal (C/M) using an active element such as Ti is known to enhance interface strengths by forming interface layers.[1] The interface strength in the C/M joint depends in a very complex way on the residual stress state, interface microstructure, interface chemistry, etc. For example, strengths of the ZrO_2/Ag–Cu–Al–Ti joints increased with the formation of Cu_3Ti_3O layer at the C/M interface, but subsequently decreased with the additional formation of TiO.[2] On the other hand, segregation of S to Al_2O_3/NiCrAl alloy interfaces caused delamination of the ceramic coating.[3] In the present work, interfacial microstructure and segregation of residual impurities to C/M interface received particular attention among the many factors which can possibly influence the C/M interface strengths.

2 EXPERIMENTAL PROCEDURE

Zirconia powders stabilized with 3 mol% Y_2O_3 were sintered for 3 h at 1773 K to produce TZP (tetragonal zirconia polycrystals) whose properties are shown in Table 1. The braze alloy with the composition of 51·6 Ag–34·9 Cu–8·7 Al–4·8 Ti (atomic %) was prepared from high purity base metals by induction melting under $2{\cdot}7 \times 10^{-1}$ Pa, and subsequently cold rolled to 150 μm. The amounts of residual S in the braze alloy and base metals are given in Table 2. The filler metals were sandwiched between ZrO_2 pellets and brazed under $2{\cdot}7 \times 10^{-3}$ Pa vacuum according to the heat treatment shown in Fig. 1. Three brazing temperatures (1223, 1243 and 1273 K) and three brazing times (0, 20 and 60 minutes) were chosen. Interfacial properties of the C/M joints were examined by scanning electron microscopy (SEM), glancing angle X-ray (with the incident angle of 5°), and Auger electron spectroscopy (AES). Finally, flexural strengths (*FS*) were measured by conducting the four-point bend tests of C/M/C specimens. Experimental details are described extensively in Ref. 4.

3 RESULTS AND DISCUSSION

As reported elsewhere,[5] there are three types of microstructure at the C/M interface, and Fig. 2 shows a typical micrograph of each microstructure. The type 'A' microstructure consists of a $Cu_2(Ti, Al)_4O$ layer which is about 0·3–0·4 μm thick and the braze alloy showing off-eutectic microstructure. In the type 'C' microstructure, which was observed at higher brazing temperatures and

Table 1. The characteristics of ZrO_2 used in this experiment

Grain size	Crystal structure	Flexural strength	Fracture toughness
0·45 μm	Tetragonal	692 ± 90 MPa	5·15 ± 0·12 $MPam^{1/2}$

Table 2. The amount of residual S in the braze alloy and base metals used

	Braze alloy	Ti	Cu	Al	Ag
S (ppm)	6	13·5	13·3	4·5	4·4

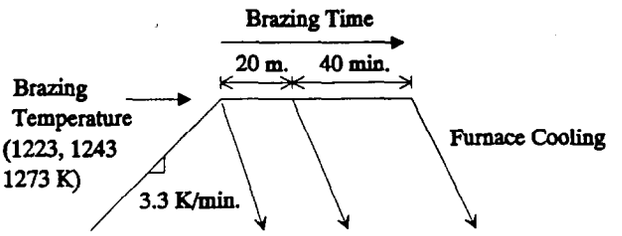

Fig. 1. Heat treatment cycle used in the brazing process.

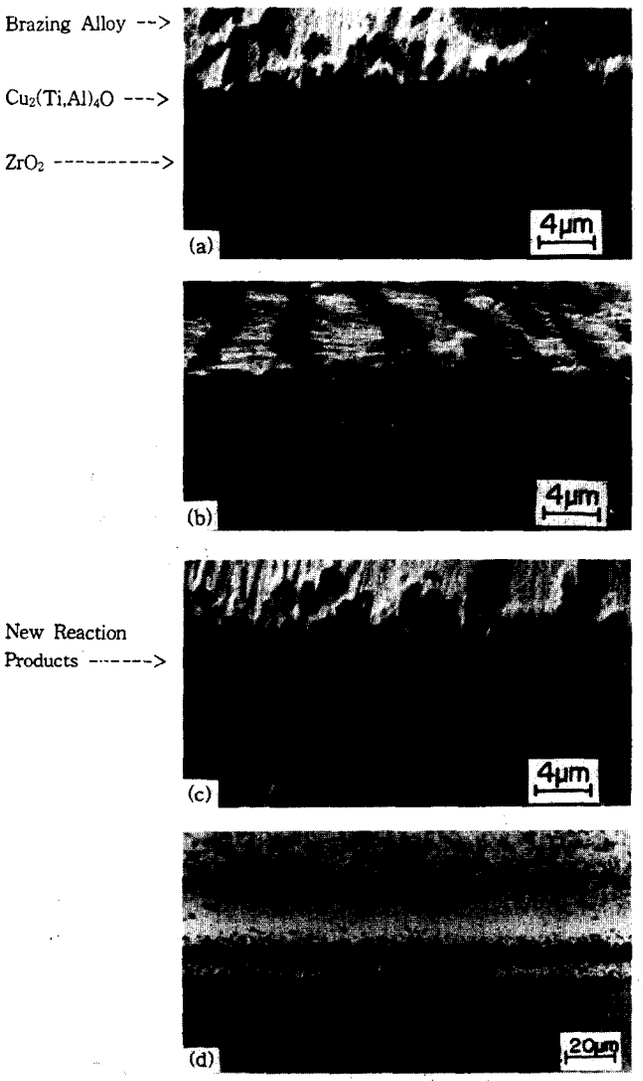

Fig. 2. SEM micrographs showing typical (a) 'A', (b) 'B', (c) 'C', and (d) 'C' microstructures. In (d), specimens in (c) were angle lapped and the thickness of the layers appearing in (d) are exaggerated.

longer brazing times, two new layers identified as γ-TiO and α-Al_2O_3 were added and the whole structure can be described as ZrO_2/γ-TiO/α-Al_2O_3/Cu_2 $(Ti,Al)_4O$. The type 'B' microstructure corresponds to a transitional stage between type 'A' and 'C', where discontinuous islands of γ-TiO/α-Al_2O_3 layers nucleated at the ZrO_2/$Cu_2(Ti,Al)_4O$ interface. Reaction products formed at the C/M interfaces at various processing conditions can be classified into three microstructures and are schematically described in Fig. 3.

In Fig. 4, flexural strengths of C/M/C specimens are shown for the nine brazing conditions. Note that *FS* reaches a maximum at intermediate brazing times at 1223 K and 1243 K, but decreases monotonically with brazing time at 1273 K. Comparisons of *FS* data with the microstructural map of Fig. 3 show that *FS* increases with brazing time and temperature in the region where the type 'A' microstructure dominates but that *FS* decreases with the emergence of the type 'B' or 'C' microstructures.

Examinations of fracture surfaces by SEM and AES did not reveal significant fractographic differences among 'A' specimens but substantial differences in the segregated S content as shown in Figs

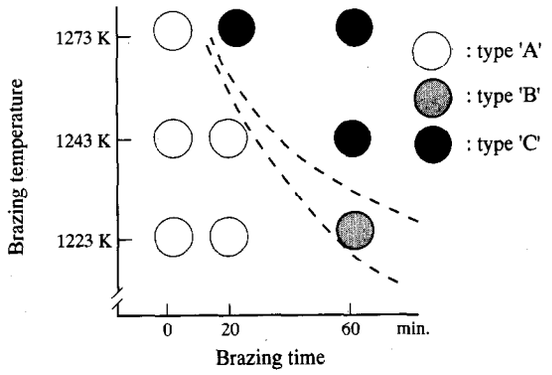

Fig. 3. A schematic diagram showing the type of interface microstructures at various brazing conditions.

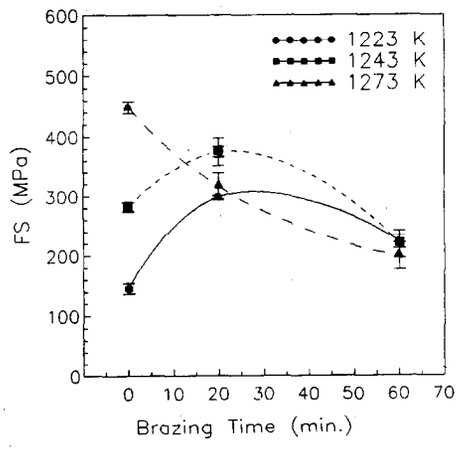

Fig. 4. Variations of flexural strength with brazing time at three brazing temperatures.

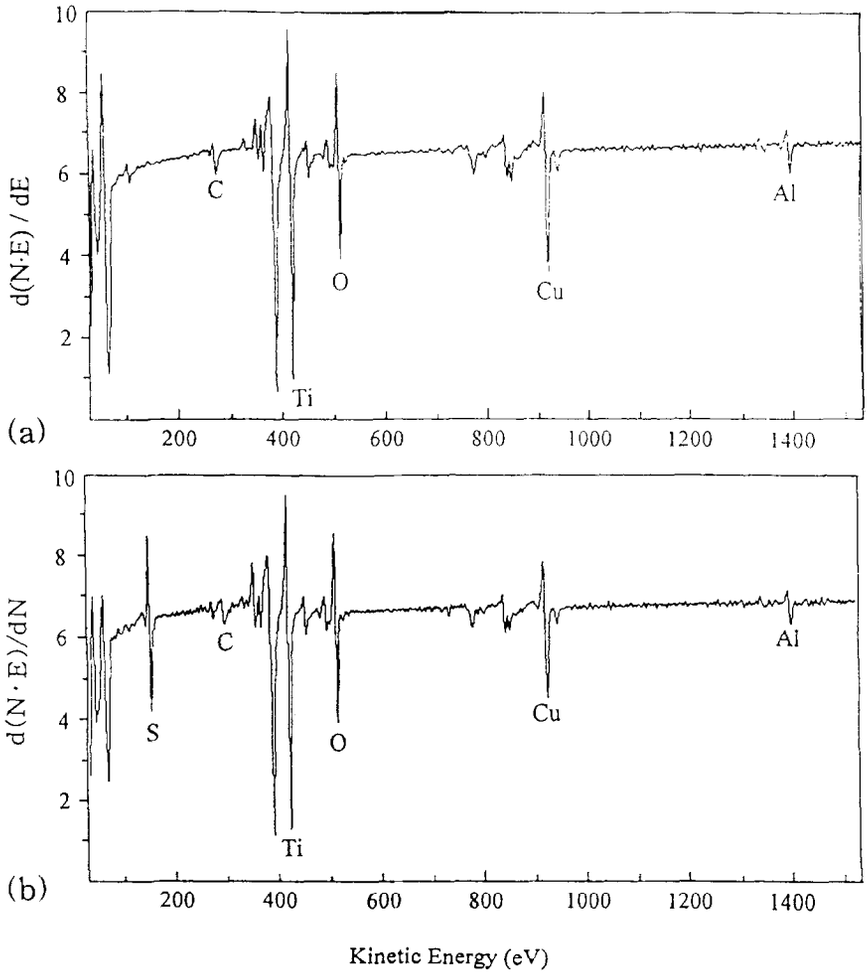

Fig. 5. Auger spectra from fracture surfaces of the 'A' type microstructure from specimens brazed for 0 time at (a) 1273 K and (b) 1223 K.

5 and 6. The S Auger peaks disappeared rapidly with subsequent sputtering which suggested that the S atoms came from the braze alloy and not from the reaction products. Among specimens with the 'A' microstructure, *FS* decreased with the S content (X_s) on $ZrO_2/Cu_2(TiAl)_4O$ interface as shown in Fig. 6, which is analogous to the grain boundary embrittlement of ferritic steel by residual impurities such as P, Sn, As, Sb and S.[5]

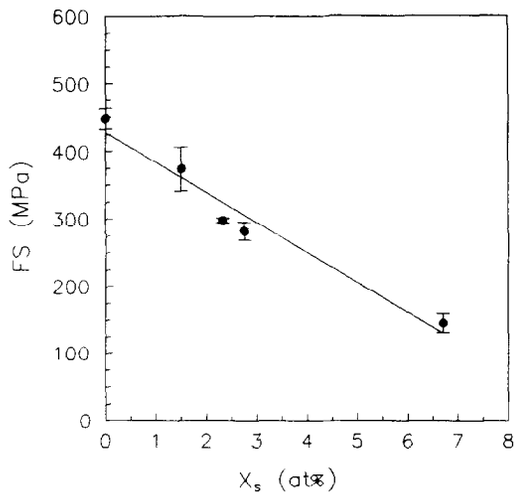

Fig. 6. Variations of the flexural strength as a function of the S content on the fracture surface among the 'A' type specimens.

This clearly suggests that the presence of embrittling elements such as S at the C/M interface is a major factor determining the interface strength. It is not clear at the present moment why the S segregation occurs only in the type 'A' microstructures and why it decreases with brazing time. The presence of a brittle phase at the C/M interface is expected to decrease *FS*, and that was the case for the TiO/Al_2O_3 layer at the ZrO_2/Cu_2 $(Ti,Al)_4O$ interface. Microhardness measurements of $Cu_2(Ti,Al)_4O$, TiO/Al_2O_3, and ZrO_2 phases listed in Table 3 show that the TiO/Al_2O_3 phase is the hardest of the three. Therefore, the thickness of the TiO/Al_2O_3 layer (X_t) at the ZrO_2/Cu_3 $(Ti,Al)_4O$ interface was measured for the 'C' type specimens and correlated with *FS* in Fig. 7. It can be seen that *FS* decreases with the thickening of the brittle TiO/Al_2O_3 layer.

Table 3. Vicker's hardness values of several phases existing near C/M interfaces

$Cu_2(Ti,Al)_4O$	Al_2O_3/TiO	ZrO_2
1390 ± 168	4559 ± 880	2534 ± 257

So far, we have demonstrated that the two main factors affecting the interface strength are the S content (X_s) and the thickness of the TiO/Al_2O_3 layer (X_t) at the ZrO_2/Cu_2 $(Ti,Al)_4O$ interface. Are there any other factors with more deleterious effects? We can eliminate the possibility as follows. Firstly, make a hypothesis that *FS* is a function of X_s and X_t only. Then,

$$FS = f(X_s, X_t) \tag{1}$$

where f is an unknown function.[6] For small X_s and X_t, we can write

$$FS = f(X_s = 0, X_t = 0) + [\frac{\partial f}{\partial X_s}]_{X_t} dX_s + [\frac{\partial f}{\partial X_t}]_{X_s} dX_t \tag{2}$$

ignoring the higher order terms. Secondly, we show that measured *FS* can be well explained in terms of eqn (2). From Figs 6 and 7, we can rewrite eqn (2) as

$$FS = 443{\cdot}8 - 44{\cdot}3\ X_s - 222{\cdot}3\ X_t \tag{3}$$

where units of *FS*, X_s and X_t are given in MPa, atomic %, and μm, respectively. In Fig. 8, *FS* values calculated from eqn (3) are correlated with experimentally measured *FS* values, and our hypothesis is justified.

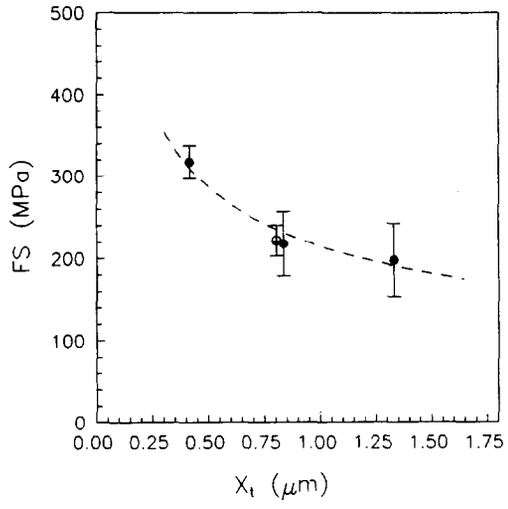

Fig. 7. Variations of the flexural strength as a function of the thickness of TiO/Al_2O_3 layer among the 'C' specimens.

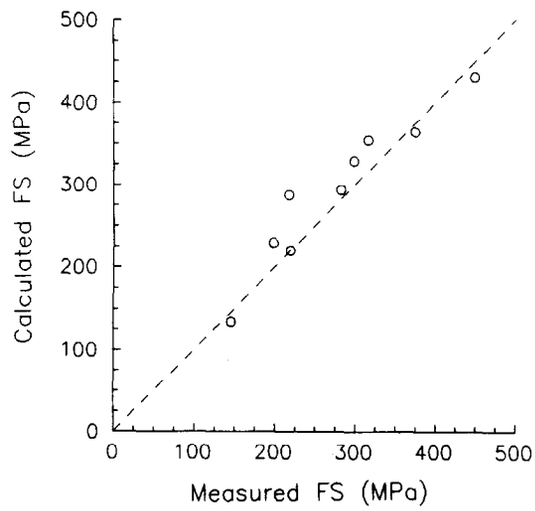

Fig. 8. Comparisons of calculated flexural strength using eqn (3) and experimental data.

4 CONCLUSION

The interface microstructures of ZrO_2/Ag–Cu–Al–Ti joints, are basically $ZrO_2/Cu_2(Ti,Al)_4O$ or ZrO_2/γ-TiO/α-$Al_2O_3/Cu_2(Ti,Al)_4O$ types which depend sensitively on the brazing temperature and time. Two main factors detrimental to the interface strength are the amount of S segregation at the C/M interface and the thickness of the TiO/Al_2O_3 layer. Thermodynamics of the S segregation are not clear at the present moment.

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