

## The Influence of Impurities on Fracture Energy of Metal-Ceramic Interfaces

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### 1. Introduction

In both the practical and theoretical aspects of joining metals to ceramics the influence of impurities on the interfacial bond strength is not fully understood. In the present paper we describe part of a study in which the interface of niobium-sapphire bicrystals was contaminated under defined conditions and the interfacial fracture energy of these UHV diffusion bonded bicrystals was determined as a measure of their bond strength (1). The model combination niobium-sapphire shows at high temperatures a simple reaction in which alumina is dissolved into niobium without any formation of an interlayer between both materials. Furthermore, niobium and sapphire are characterized by nearly the same expansion behavior which minimizes the development of thermal stresses during cooling down from the bonding temperature. In the following we report on experiments in which silver or titanium atoms have been chosen as interfacial impurity elements. Silver is practically insoluble in niobium and sapphire whereas titanium possesses a highly negative free enthalpy of oxide formation. It is assumed that both these properties are associated with interfacially active elements in the system niobium-sapphire.

### 2. Experimental Procedure

The chemical composition of the single crystals niobium and sapphire is given in Table 1. The bicrystals were manufactured in an UHV machine (Fig. 1) which consists of three separately pumped chambers (2). The specimen preparation chamber is used to clean the surfaces of the

crystals by argon ion bombardment and to analyse their impurity content by means of an Auger spectrometer. In the doping chamber the impurity elements silver or titanium are evaporated onto the sputter-cleaned surface of the sapphire single crystals prior to bonding. The layer thicknesses range from a fraction of a monolayer up to several microns. A carriage on wheels and

Table 1. Impurity Content of the Niobium and Sapphire Single Crystals

material	purity [weight %]	impurities [weight ppm]
Nb	99.999	39 O < 10 S < 5 C
sapphire	99.99	< 100 Mg < 20 Ca

special manipulators are used to transport the specimens from one chamber to the others. In the welding chamber the specimens are stacked onto each other in the sequence alumina end piece, niobium crystal, sapphire crystal, niobium crystal and upper alumina endpiece using a special device by which one niobium crystal and the sapphire crystal can be brought into the desired mutual crystallographic orientation. Welding takes place in the upper part of the chamber by means of a molybdenum susceptor which is heated by an RF coil. In most of our experiments diffusion bonding was carried out at 1400°C for 3 hours under a compressive stress of 10 MPa. The minimum vacuum

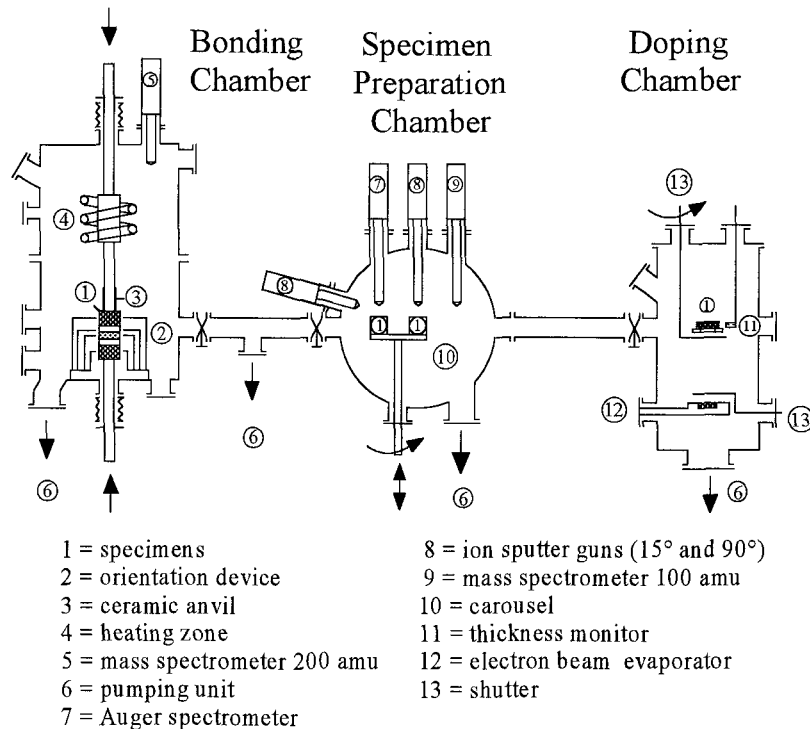


Fig. 1 Ultrahigh vacuum diffusion bonding apparatus

pressure was  $1 \times 10^{-10}$  mbar. During welding the vacuum pressure increased to  $1 \times 10^{-8}$  mbar. After bonding bend test specimens of  $2 \times 4 \times 36$  mm<sup>3</sup> were cut from the welded pieces. They consist of one Nb crystal welded to the Nb-sapphire bicrystal in the middle and the two polycrystalline alumina end pieces of 15 mm to the left and right of the crystals. The thickness of each of the bonded metal and ceramic crystals is 2 mm. The specimens were notched at the metal-ceramic interface of the bicrystal and the interfacial fracture energy  $\bar{G}_C$  was determined in a four-point bend test at a constant crosshead velocity of 96.8  $\mu\text{m}/\text{min}$  according to a method described by Suga (3).

Experiments to analyse the fractional interface and surface coverage of the impurity atoms were

performed in a separate Auger spectrometer (SAM 500, Perkin-Elmer) using bend test specimens which were cut from bonded pieces and in situ fractured in the AES device.

### 3. Results and Discussion

Four different crystallographic orientations O1 to O4 of the interface of the bicrystals were studied. They are given in table 2. The orientation of the two bonded crystal lattices has a strong influence on the fracture resistance of the undoped interface as shown by Fig. 2. Bicrystals of orientation O4 produce the toughest interfaces with  $\bar{G}_C = 2107$  J/m<sup>2</sup> while bicrystals of orientation O2 only have a interface fracture resistance of 77 J/m<sup>2</sup>. The bicrystals O3 and O4 show considerably higher interface toughness data than the O1-O2 group. O1 and O2 differ from O3 and O4 in the orientation of the metal

side of the interface. In both both groups a change in sapphire orientation leads to alteration of  $\bar{G}_c$ . These results indicate that the fracture toughness of the interface is affected by two interrelated quantities: (i) by the work of adhesion which depends on the interface orientation and (ii) by the plastic work in the adjacent metal which is dissipated in a magnitude depending on the position of its glide planes and glide directions relative to the interface and to the crack propagation.

Table 2 Crystallographic Orientation of Niobium-Sapphire Bicrystals

Type	Orientation
O 1	Nb(100)[001]  Saphir (11 $\bar{2}$ 0)[0001]
O 2	Nb(100)[001]  Saphir (1 $\bar{1}$ 00)[11 $\bar{2}$ 0]
O 3	Nb(110)[001]  Saphir (11 $\bar{2}$ 0)[0001]
O 4	Nb(110)[001]  Saphir (0001)[1 $\bar{1}$ 00]

The interface fracture energy of bicrystals of orientations O3 and O4 as a function of the fractional interface coverage of silver  $\Theta_{Ag}$  is given in Fig. 3. Fig. 4 shows a plot of  $\bar{G}_c$  versus  $\Theta_{Ag}$  for bicrystals of orientations O1 and O2.

By doping with silver  $\bar{G}_c$  is strongly decreased. The effect is more pronounced for the orientations O4 and O3 with the higher fracture energy of the undoped interface. The fracture energy is assumed to depend nonlinearly on the work of adhesion:  $\bar{G}_c = W_{ad} + W_p(W_{ad})$  where  $W_p$  is the dissipated work of plastic deformation of the metal part and  $W_p = (W_{ad})^n$  (4). Therefore, a given decrement of the work of adhesion should lead to a larger reduction of  $\bar{G}_c$  for a strong interface than for a weaker one. According to a pair bonding model originally proposed by Seah (5), which was modified to include metal-oxygen

bonds, cohesion is reduced by segregants which have a larger atomic radius, a lower heat of sublimation and a lower heat of sublimation of their oxides than the bulk material. Silver fulfills these conditions in agreement with the experimental observations. The atomic radii of Nb and Ag are similar but the heat of sublimation of silver is much smaller than that of niobium. The same is true for the oxide sublimation enthalpies. Moreover, the AES analyses showed that the impurity atoms silver and titanium can only be detected at the metal side of the interface fracture. This result facilitates estimates based on the modified pair bonding model: only Nb-O and Ag-O or Ti-O bonds have to be considered.

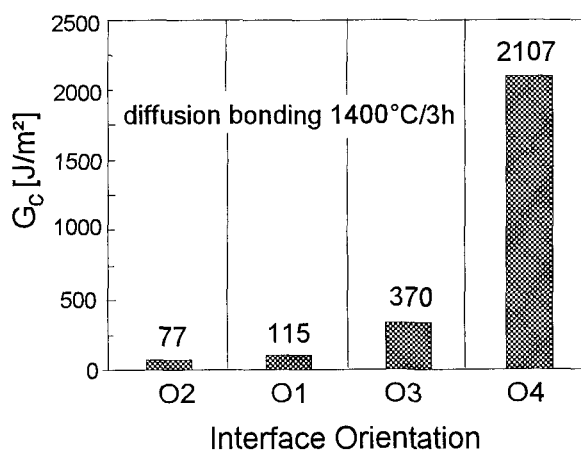


Fig. 2. Fracture energy  $\bar{G}_c$  as a function of the crystallographic orientations O1 to O4 of undoped niobium-sapphire interfaces

The interface fracture energy  $\bar{G}_c$  of Nb-sapphire bicrystals of orientation O1 bonded at 1300°C for 1h is given together with the initial titanium layer thickness before bonding as a function of the fractional interface monolayer coverage of titanium  $\Theta_{Ti}$  in Fig. 5.  $\bar{G}_c$  increases from 160 J/m<sup>2</sup> for the pure interface to 740 J/m<sup>2</sup> for a Ti-doped interface with a

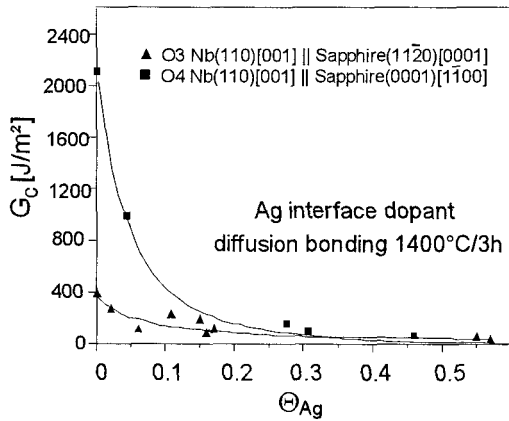


Fig. 3. Fracture energy  $\bar{G}_c$  of Nb-sapphire bicrystals as a function of the fractional interface coverage of silver  $\theta_{Ag}$

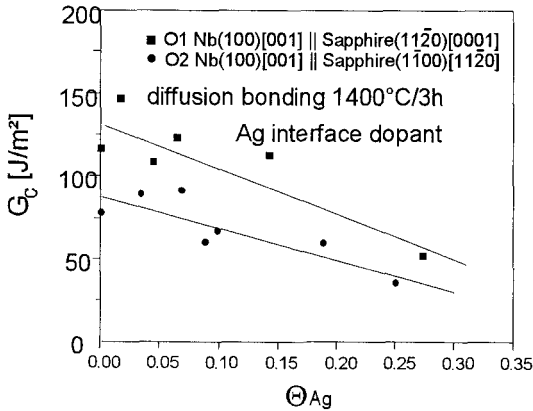


Fig. 4. Fracture energy  $\bar{G}_c$  of Nb-sapphire bicrystals of orientations O1 and O2 as a function of the interface fractional interface coverage of silver  $\theta_{Ag}$

fractional coverage  $\Theta_{Ti}$  of 0.62. If the interaction of titanium with the oxygen of sapphire is taken into consideration as in the modified pair bonding model the work of adhesion and hence the fracture energy will be increased due to the fact that the enthalpy of formation of Ti-O bonds is larger than that of Nb-O bonds.

Since the interface coverage with silver atoms  $\Theta_{Ag}^b$  was quantitatively determined for different crystallographic orientations of niobium-sapphire bicrystals, the change in the work of adhesion  $\Delta W_{ad}$  and hence  $\bar{G}_c$  as a function of  $\Delta W_{ad}$  can be calculated from these data using a thermodynamical theory of Rice and Wang (6).

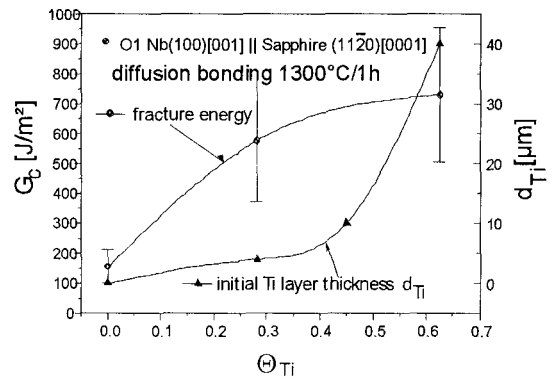


Fig. 5. Fracture energy  $\bar{G}_c$  of Nb-sapphire bicrystals of orientations O1 as a function of the interface fractional interface coverage of titanium  $\theta_{Ti}$

From AES spectra taken from bonded and unbonded sites at the niobium side of the interface fractures the ratio  $a_{Ag}$  between the fractional surface and interface coverage was determined. The ratio  $a_{Ag}$  was 3.46 for silver on (100) Nb planes of bicrystals of orientations O1 and O2 and 1.75 for silver on (110) Nb planes of bicrystals of orientations O3 and O4. Thus, silver showed a larger enrichment of atoms at the surface than at the interface which is typical for an impurity element which reduces the adhesion. Assuming that the impurity concentration remains unchanged after interface fracture and as observed, that the impurity atoms are only present at the niobium site of the interface fracture the change in the work of adhesion is

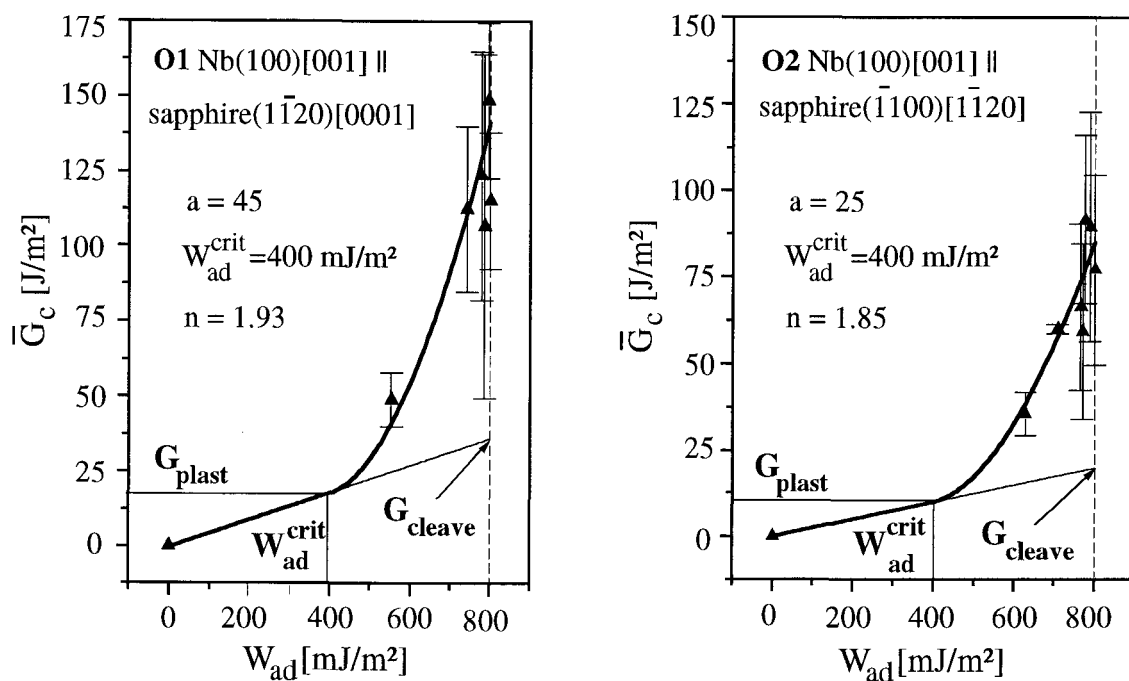


Fig. 6. Interface fracture energy as a function of the work of adhesion for orientations O1 and O2

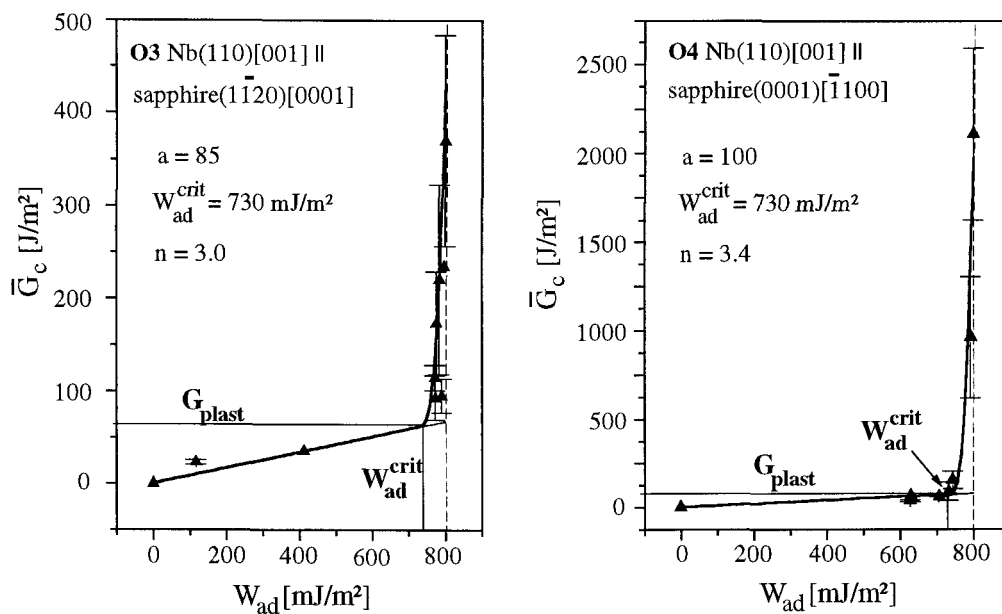


Fig. 7. Interface fracture energy as a function of the work of adhesion for orientations O3 and O4

given by

$$\Delta W_{ad}(\Theta_{Ag}) = RT\Theta_{Ag}\Gamma_{Ag}^{b0} \cdot \ln \left[ \frac{1 - a_{Ag} \cdot \Theta_{Ag}}{a_{Ag} \cdot (1 - \Theta_{Ag})} \right]$$

where  $\Gamma_{Ag}^{b0}$  is the maximum number of Ag atoms per unit area. To establish a relationship between the interface fracture energy  $\overline{G}_C$  and the work of adhesion  $W_{ad}$  we used a theoretical value for the work of adhesion of the pure niobium-sapphire interface of 800 mJ/m<sup>2</sup> (7). Preliminary results of Jilavi (8) for a uncontaminated interface of orientation O3 give an experimental value of the work of adhesion of  $W_{ad} = 954$  mJ/m<sup>2</sup>. For the crystallographic orientations O1 to O4 of the niobium-sapphire bicrystals the interface fracture energy  $\overline{G}_C$  is given in Figs. 6 and 7 as a function of the work of adhesion  $W_{ad}$  for which  $\Delta W_{ad}$  was calculated from the experimental data of the interface and surface coverage of silver. It can be seen that the interface fracture energy  $\overline{G}_C$  increases linearly up to a critical value of the work of adhesion

$W_{ad}^{crit}$ . Above this value a strong exponential increase in  $\overline{G}_C$  occurs which is due to extensive plastic deformation of the metal regions adjacent to the crack. The obtained empirical relationship between the interface fracture energy  $\overline{G}_C$  and the work of adhesion  $W_{ad}$  can be described by

$$\begin{aligned} \overline{G}_C &= G_{cleave} = a \cdot W_{ad} && \text{for } W_{ad} < W_{ad}^{crit} \\ \overline{G}_C &= a \cdot W_{ad} + (W_{ad} - W_{ad}^{crit})^n && \text{for } W_{ad} > W_{ad}^{crit} \end{aligned}$$

where  $G_{cleave}$  is the cleavage energy and  $a$  is a factor depending on the crystallographic orientation of the bicrystal. The exponent  $n$  is a function of the orientation of the metal part. A value of  $n = 1.9$  was obtained for (100) interface

planes of niobium. It increases to about  $n = 3$  for (110) interface planes of niobium. The critical energy release rate  $G_{plast}$  for the onset of gross plastic deformation in the metal is proportional to  $W_{ad}^{crit}$ :

$$G_{plast} = a \cdot W_{ad}^{crit}$$

On the niobium side of the interface fracture glide steps were detected and crystallographically identified by light optical observations using differential interference contrast (1). The amount of visible plastic deformation depends on the crystallographic orientation of the bicrystal and will be reduced if the fractional interface coverage of silver atoms is increased.

Brittle interface fracture will be favored if the work of adhesion of the metal-ceramic bicrystal is low as in the case of highly silver-doped interfaces and the yield stress of the metal is comparatively high. However, ductile interface fracture will occur if the work of adhesion is high and the metal possesses a low yield stress.

#### 4. References

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