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Joining of zirconia using zirconium-based alloys

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The contact angles of Zr–Ni, Zr–Cu and Zr–Co alloys against PSZ were measured by the sessile drop method. Each alloy wetted PSZ very well. Zr–Co alloys showed a different behaviour. Joints of PSZ plates were obtained using Zr–17Ni alloy. At the joint interface, internal oxidation of zirconium occurred. The fracture shear strength of this joint was 55 MPa.

1. Introduction

Ceramics have been widely used in severe environments because of their excellent chemical, heat and wear resistances. The recent production of high-performance ceramics has enabled them to be applied in many fields. However, many mechanical and thermal problems of ceramics remain unsolved for wider application to structural materials. Joining ceramics to ceramics or to metals is a new design technology for overcoming the inherent disadvantages of ceramics.

Fully stabilized zirconia (FSZ) is applied as an oxygen sensor to solid electrolytes but partially stabilized zirconia (PSZ) has the strongest and toughest properties. Therefore, PSZ has been expected to be widely applicable as structural materials.

Some investigations regarding joining of zirconia have been carried out. Successful diffusion bonding of FSZ to metals such as copper [1], nickel [1] and platinum [2, 3] has been demonstrated. The joining of PSZ using various filler materials, such as platinum [4], nickel oxide [5], and oxide glass solder [6] has been reported. A study of diffusion bonding between PSZ and carbon steel [7] has been also carried out. Many presentations [8] regarding ceramics joining have used titanium-containing silver-based active brazing alloy. Few joints of PSZ have been obtained using zirconium-based active filler metal.

In the present study, the wettability of Zr–Ni, Zr–Cu and Zr–Co alloys against PSZ was examined. In addition, we attempted to join PSZ using Zr–Ni alloy and to characterize the interface of the joint using various methods such as X-ray diffraction (XRD), scanning electron microscopy (SEM), electron probe X-ray microanalysis (EPMA), and X-ray photoelectron spectroscopy (XPS).

2. Experimental procedure

The samples of PSZ were prepared by sintering at 1573 K for 7.2×10^3 s in air. The density was 6.08 g cm^{-3}, and the chemical compositions of the raw materials are shown in Table I. Square PSZ plates, 10 mm × 10 mm and 4 mm thick were polished with 3, 1 and 1/4 μm diamond paste after grinding with nos 100, 600 and 1000 diamond wheels.

The zirconium alloy samples were prepared by melting suitable mixtures of zirconium (99.95% pure), nickel (99.99% pure), copper (99.99% pure) and/or cobalt (99.99% pure) in an arc furnace in water-cooled copper crucibles. The arc heating conditions were 20 V × 150 mA in an argon (99.999% pure) atmosphere (1.2×10^5 Pa) after evacuating to less than 4×10^{-3} Pa. The compositions of the zirconium alloys are shown in Table II. Each alloy sample was cut into small pieces weighing about 0.1–0.5 g.

After preparation, the specimens were ultrasonically washed in acetone and dried well.

Various methods (e.g. [9]) for measuring the wettability of molten metals against the ceramics have been reported. In this study, the wettability of molten zirconium alloys against PSZ was measured by the sessile drop method. Sessile drop observations were

TABLE I (a) The chemical compositions (wt %) of zirconia powder[a] and (b) mechanical properties of sintered PSZ

(a)

ZrO_2	Y_2O_3	HfO_2	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	Na_2O	i.g. loss
93.2	5.30	0.86	0.005	0.004	0.005	0.004	0.005	0.50

(b)

Bending strength (MPa)	Fracture toughness (MN m^{-2})	Hardness (H_v)
1000	8	1300

[a] OZC-3YA.

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TABLE II The compositions (wt%) and melting point of the zirconium alloys

Alloy	1	2	3	4	5	6	7	8	9	10	11
Zr	83.0	73.4	13.0	79.0	63.0	53.0	47.0	9.0	85.0	74.0	57.5
Ni	17.0	26.6	87.0								
Cu				21.0	37.0	47.0	53.0	91.0			
Co									15.0	26.0	42.5
m.p. (K)	1237	1283	1443	1269	1202	1164	1159	1239	1234	1334	1585

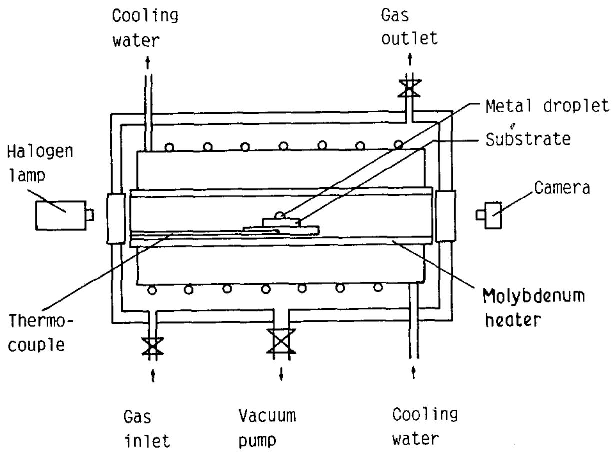


Figure 1 Schematic diagram of the experimental apparatus for measurement of the contact angle.

made in a molybdenum tube resistance furnace (Fig. 1) operated at less than 5×10^{-3} Pa using zirconium metal as an oxygen getter. The heating rate was 3.33×10^{-2} K s^{-1}. After melting the drop, the photography was begun. For the Zr–Cu alloy, the temperature was kept constant during measurement after it was raised to the required temperature.

In addition, the wettability of silver (99.99% pure) and copper (99.99% pure, oxygen free) against PSZ was measured as a reference.

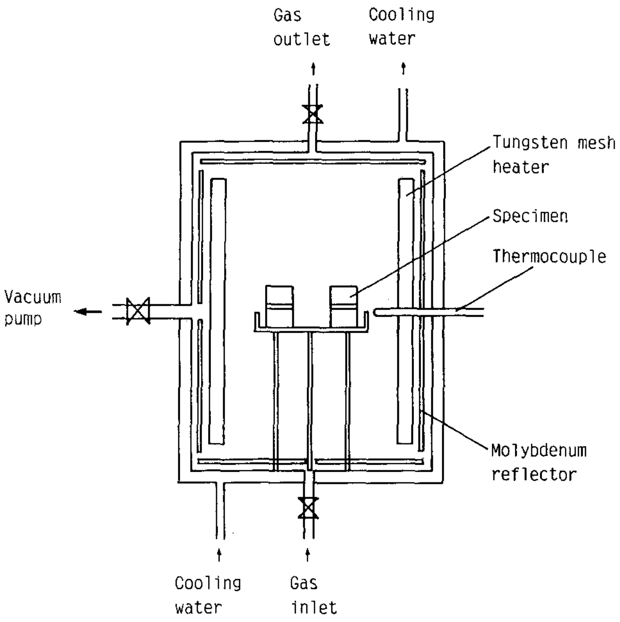


Figure 2 Schematic diagram of the experimental apparatus for joining.

The photographs of each drop were enlarged and the shape was read using a digitizer.

In general, Bashforth and Adams method [10] was used to calculate the contact angles. The curve-fitting method [11] was also used as a computer numerical

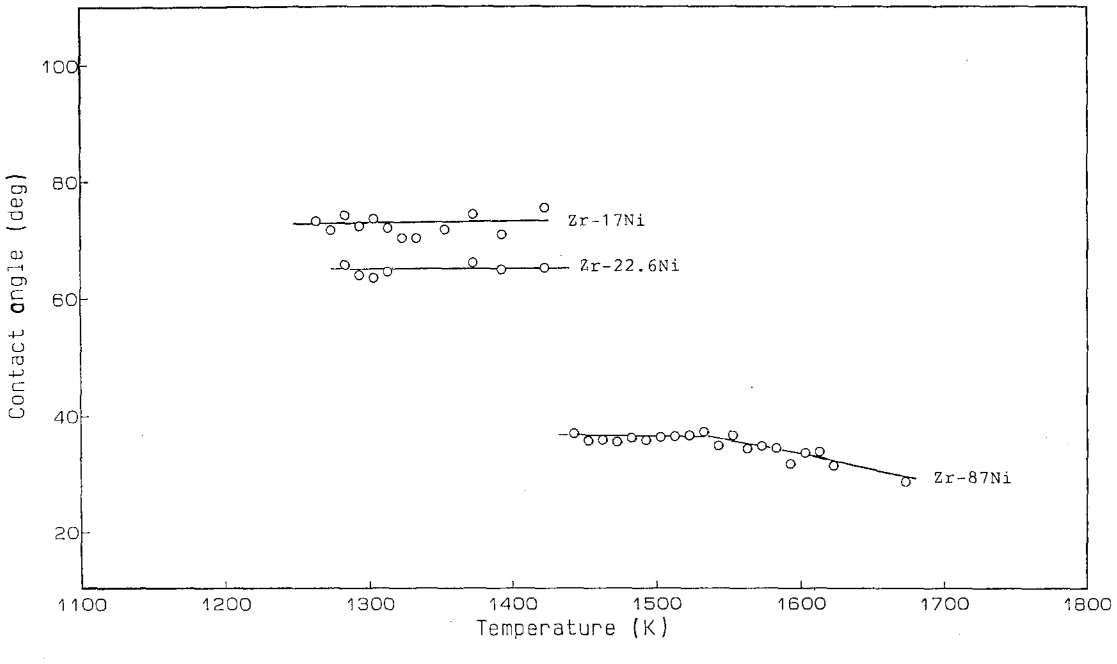


Figure 3 Temperature dependence of the contact angle for Zr–Ni alloy against PSZ.

anlysis. In the present study, the contact angle was calculated by a non-linear least squares method where the shape of a drop was approximated by a circle.

Joining of PSZ plates was performed using Zr–17 Ni alloy. A Zr–17 Ni plate (10 mm × 10 mm × 0.5 mm) was placed between the PSZ plates, and joining was carried out by heating at 1273 K for 1.8×10^3 s under a vacuum (2×10^{-3} Pa). No external pressure was applied in joining the pair. The experimental apparatus is shown in Fig. 2.

In order to characterize the reaction region, XRD, SEM observation, EPMA and XPS analyses were performed. XRD analysis was performed on fractured surfaces of the joint in order to identify crystalline phases precipitated in the interlayer of the joint. Each fractured surface was ground away by a few micrometres, and then XRD analysis was repeated with the newly exposed surface. XRD patterns were measured with CuK_α radiation using a diffractometer (Rigaku Co./Rotaflex RAD-RC System) operated at 40 kV and 100 mA, and a scan speed of 4° min^{-1} in 2θ.

The joined interlayer was observed by SEM and analysed using EPMA or EDX. SEM observations, EPMA and EDX analyses were performed using JXA-8600 M type or JSM-T20 type (Jeol) microscope operating at 15 or 20 kV.

XPS of the zirconia surface was performed using ESCA Lab-5 system (VG Scientific Co.). The charging effect was corrected using the C′1s peak position (284.6 eV) as standard.

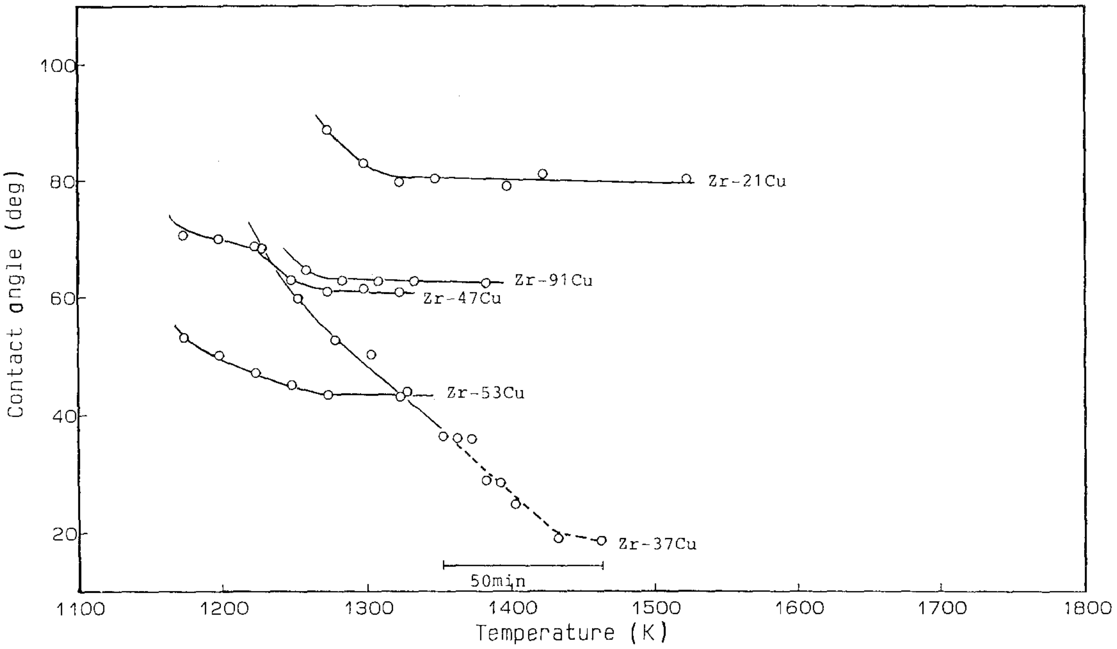


Figure 4 Temperature dependence of the contact angle for Zr–Cu alloy against PSZ.

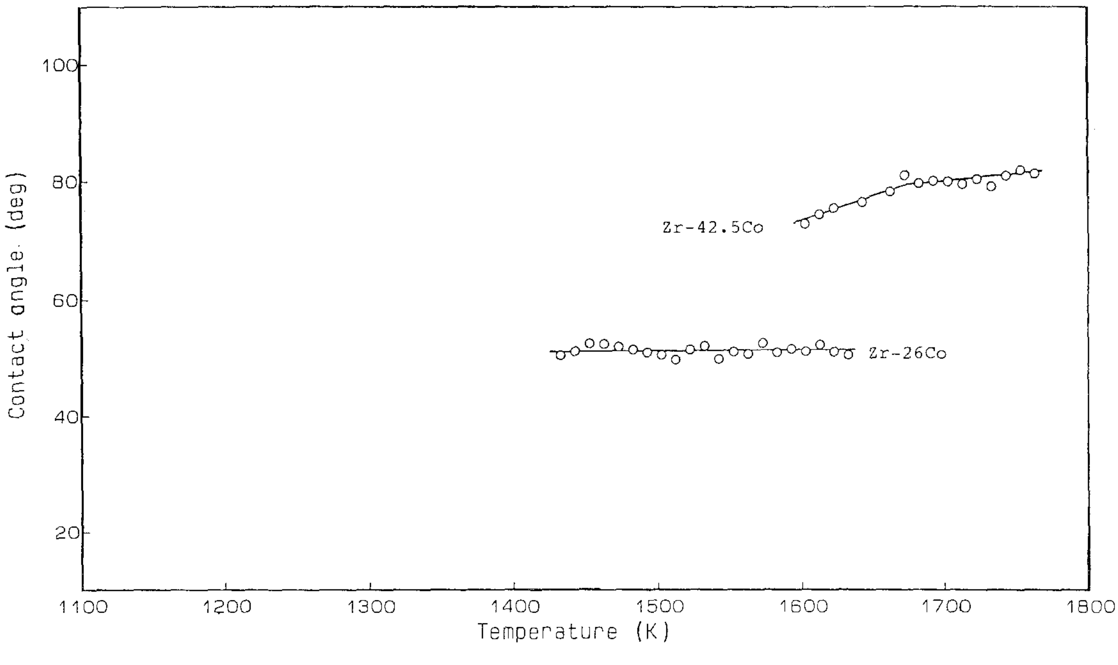


Figure 5 Temperature dependence of the contact angle for Zr–Co alloy against PSZ.

3. Results and discussion

3.1. Wettability of zirconium alloy against PSZ

The colour of each PSZ sample after the runs changed from white to black. Before and after the experiment, no transformation of the crystalline phase could be confirmed in PSZ by XRD.

The contact angles of both silver and copper against PSZ were 110°–120° at 1300–1630 K, and were little affected by temperature. Ueki *et al.* [12] reported that the contact angles of silver and copper against zirconia were 126°–116° and 129°–120° at 1373–1473 K, respectively. In addition, Humenik and Parikh [13] reported that the contact angle of nickel against zirconia was 110°–120° at 1773 K.

In this paper, the contact angles of zirconium alloys against PSZ were less than 90°. These results suggest that zirconium alloys are wettable to zirconia and effective in the joining of zirconia.

SEM observation revealed that both silver and copper drops produced no reaction layer in the interface with PSZ. On the otherhand, a reaction layer was observed for each zirconium alloy. Therefore, it is considered that the addition of zirconium to the alloy produced some reaction products which made the drop wettable.

Fig. 3 shows the temperature dependence of the contact angle for Zr–Ni alloy against PSZ. On decreasing the content of zirconium, the contact angle was decreased. It is considered that the thick reaction layer inhibited wetting and spreading of the drop when the zirconium content was high.

The contact angles of Zr–17 Ni and Zr–26.6 Ni drops were almost unchanged with increasing temperature. It is considered that the change in contact angle ceased almost immediately after the alloy had melted. In the case of Zr–87 Ni drops, the contact angle began to decrease at about 1530 K, suggesting that the reaction between the zirconium alloy and PSZ occurred above this temperature.

The temperature dependence of the contact angle for Zr–Cu alloy against PSZ is shown in Fig. 4. In the case of Zr–Cu drops, there was no clear relationship between zirconium content and contact angle. With increasing temperature, the contact angle decreases. In the case of Zr–87 Ni alloy, the contact angle tended to decrease at 1353 K when the temperature was kept constant. These results suggest that the reaction product layer induced accelerated wetting.

Fig. 5 shows the temperature dependence of the contact angle for Zr–Co alloy against PSZ. The contact angle of a Zr–26 Co drop was almost unchanged with increasing temperature. It is also considered that

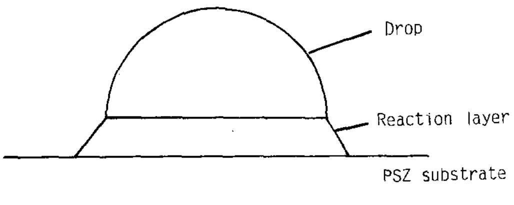


Figure 6 Schematic representation of the Zr-15Co alloy drop.

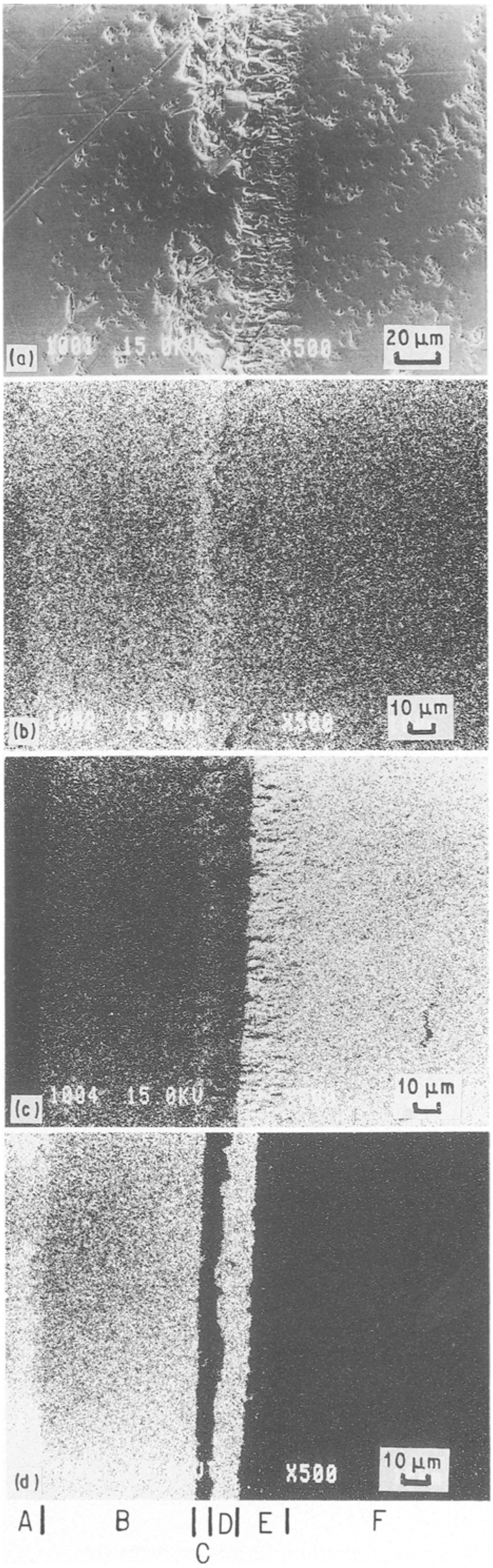


Figure 7 (a) Scanning electron micrograph and (b–d) EPMA results of the interface joined at 1273 K. (b) ZrL_α, (c) OK_α, (d) NiK_α.

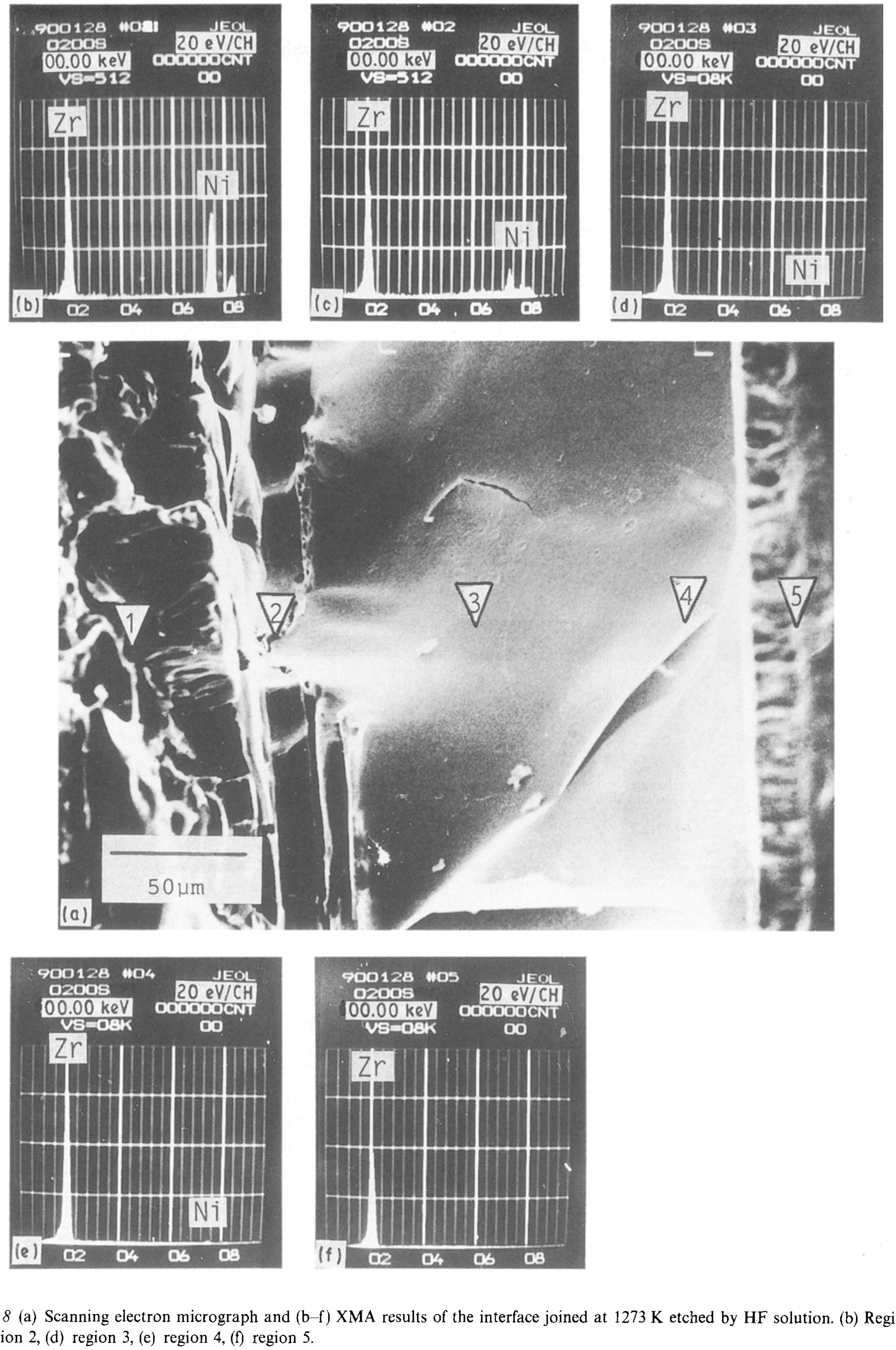


Figure 8 (a) Scanning electron micrograph and (b–f) XMA results of the interface joined at 1273 K etched by HF solution. (b) Region 1, (c) region 2, (d) region 3, (e) region 4, (f) region 5.

the change in the contact angle ceased almost immediately after the drop melted. In the case of Zr–42.5 Co drops, the contact angle increased when the temperature increased. This result was different from the other system alloys. For Zr–15 Co alloy, a reaction product layer over 100 μm thick was formed in the interface, as shown in Fig. 6, and consequently measurement and calculation of contact angles were not carried out. The same phenomenon occurred with Zr–42.5 Co drops. It is considered that the existence of a reaction layer depresses wetting and spreading of the drop, and so the contact angle is seemingly increased.

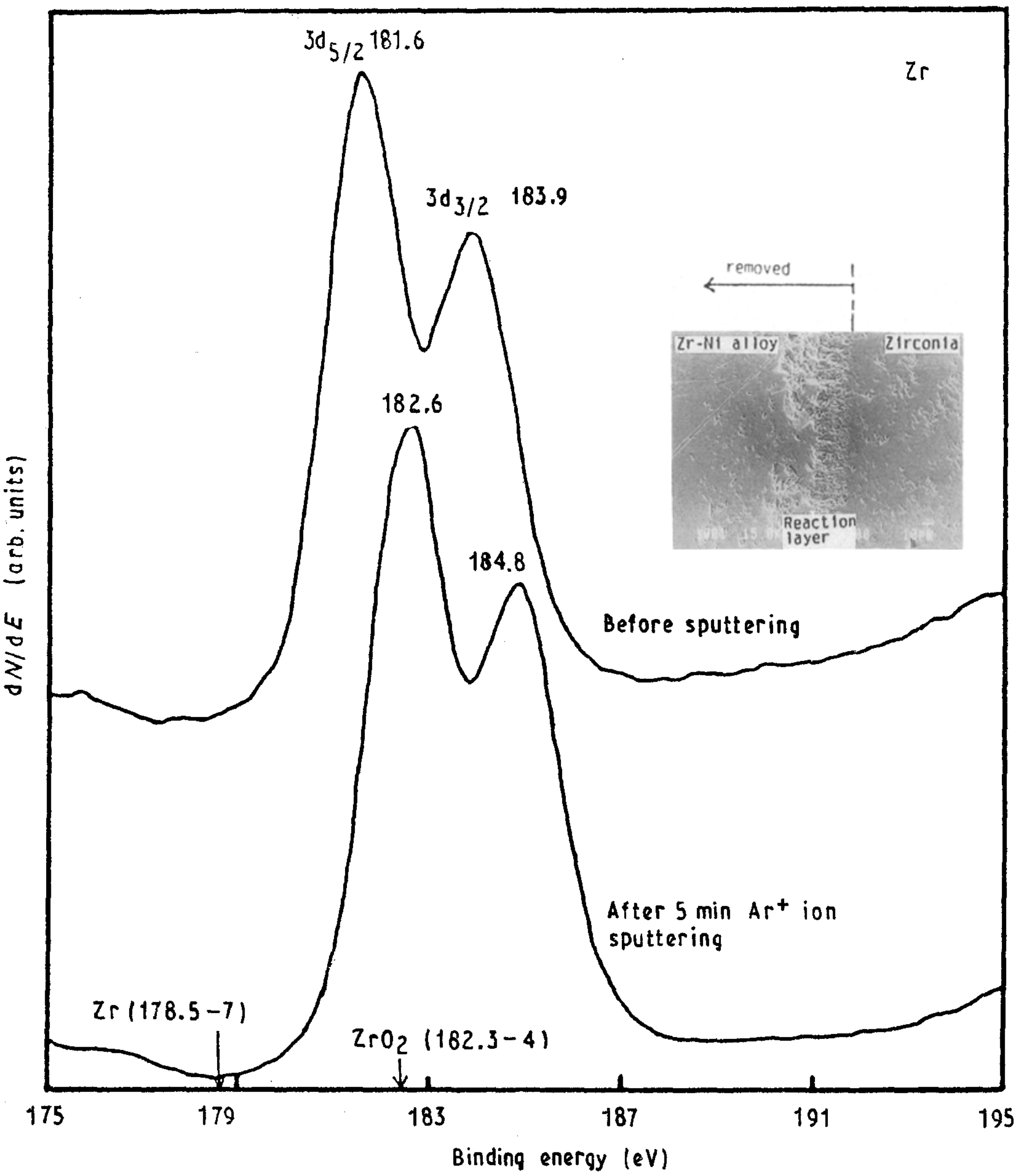


Figure 9 X-ray photoelectron spectra of Zr3d obtained from fracture surface of the joint.

In this study, it has become apparent that reaction products of Zr–Ni and Zr–Cu alloys against PSZ promote wettability, whereas the reaction product of Zr–Co alloy inhibits wetting and spreading of the drop.

3.2. Joining of zirconia using Zr–17 Ni alloy

After joining, the specimens became as black as the samples obtained in the wettability experiment. The fracture shear strength of this joint body was 55 MPa.

Secondary electron image, ZrL_α, OK_α and NiK_α X-ray images are shown in Fig. 7. It is certified that the reaction layer (region B) formed not at the zirconia side but at the alloy side, i.e. the reaction layer was deposited on the surface of PSZ. In this region, nickel did not exist, but oxygen and zirconium were confirmed. Therefore, this region was shown to be composed of zirconium oxide. In addition, nickel was not present in region D, where zirconium and a little oxygen were concentrated. It is considered that liquid-phase zirconium was oxidized internally by oxygen from the zirconia during the joining process, and was then precipitated, excluding nickel, during the cooling process.

A scanning electron micrograph of the same sample etched with HF solution, and its EDX results, are shown in Fig. 8. Regions very sparse in nickel were similarly observed (regions 3 and 4).

XPS (Zr_{3d}) of the fractured surface of the joint after removal of regions B–F (see Fig. 7), are shown in Fig. 9. These results showed that the binding energy of the region near the interface (181.6 eV) was less than in PSZ bulk (182.6 eV), and so this region was more metallic than PSZ bulk.

Fig. 10 shows XRD results of the joint interface. The peaks were identified as α-Zr and $NiZr_2$ in regions E and F (see Fig. 7), α-Zr, $NiZr_2$, $ZrO_{0.35}$, Ni–Zr–O and an unknown peak in regions C and D, and ZrO_2 in regions A and B.

It has become apparent that the zirconium composing the filler alloy was oxidized internally by zirconia during the joining process, and so produced zirconium oxide. On the other hand, it was pre-

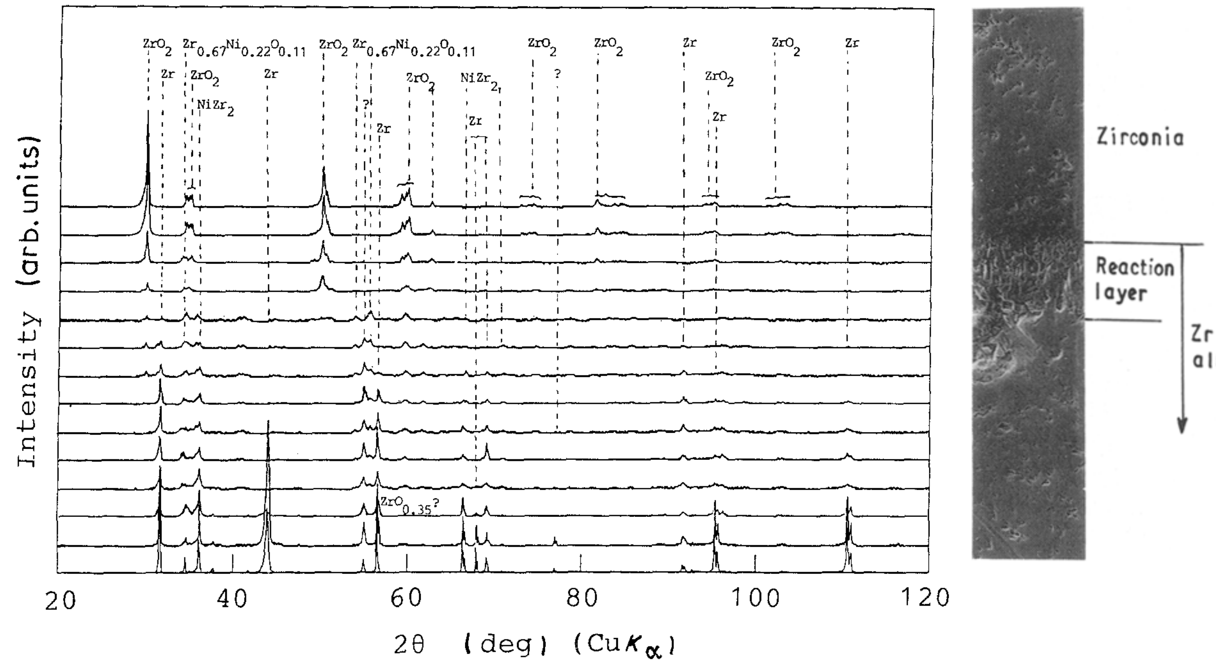
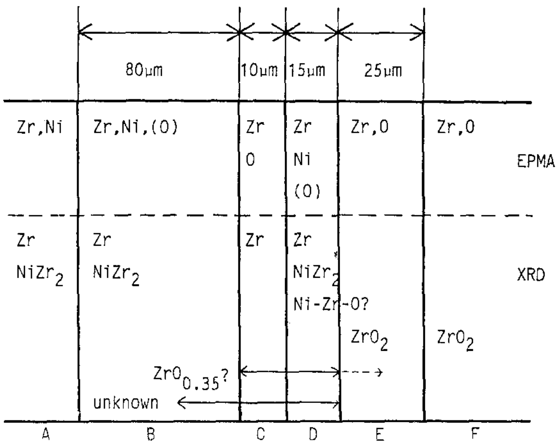


Figure 10 X-ray diffraction patterns obtained from the fracture surface of the joint.



	80µm	10µm	15µm	25µm		
Zr,Ni	Zr,Ni,(O)	Zr O	Zr Ni (O)	Zr,O	Zr,O	EPMA
Zr NiZr$_2$	Zr NiZr$_2$ ZrO$_{0.35}$? unknown	Zr	Zr NiZr$_2$ Ni-Zr-O?	ZrO$_2$	ZrO$_2$	XRD
A	B	C	D	E	F	

Figure 11 Schematic representation of the joint interface.

cipitated with the exclusion of nickel during the cooling process.

A schematic representation of the joint interface is shown in Fig. 11.

4. Conclusion

The contact angles of Zr–Ni, Zr–Cu and Zr–Co alloys against PSZ were measured by the sessile drop method. Each alloy was very wettable to PSZ, and the contact angles were less than 90°. On increasing the temperature, the contact angles decreased in Zr–Ni and Zr–Cu alloys. On the other hand, some Zr–Co alloys showed a different behaviour. It is considered that the precipitates inhibit wettability and spreading of the drop.

Joining of PSZ plates was obtained using Zr–17 Ni alloy. Internal oxidation of zirconium occurred, and the shear strength of this joint body was 55 MPa.

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