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Penetration Treatment of Plasma-Sprayed ZrO_2 Coating by Liquid Mn Alloys

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The penetration phenomena of liquid manganese (Mn) alloy into porous ZrO_2 (8 wt% Y_2O_3) coating plasma sprayed on SS400 steel substrate was studied by heating in a vacuum atmosphere. The improvement in mechanical properties of the coating by heat treatment with liquid Mn alloys was examined. Liquid Mn alloys, such as Mn-Cu, Mn-Sn, and Mn-In, rapidly penetrated the coating and formed a chemical bond between the coating and the substrate. The densification of the ZrO_2 coating occurred when ZrO_2 particles were sintered with liquid Mn alloys that penetrated the porous coating. The dense coating was free of porosity, and its hardness increased after heat treatment with Mn alloys, compared with as-sprayed ZrO_2 coating. Moreover, the fracture toughness of the coating reached the same levels as those of sintered yttria-stabilized PSZ.

1. Introduction

PLASMA-SPRAYED coatings have been widely applied in many industrial fields because of their excellent wear, erosion, heat resistance, and corrosion resistance properties. However, ZrO_2 coatings, like all ceramic coatings, exhibit connected porosity, and therefore, properties such as mechanical strength, fracture toughness, and wear resistance are diminished. The ceramic coatings also do not play an important role in protecting the metal substrate in a corrosive atmosphere under high-temperature conditions. Various methods have been reported (Ref 1-3), such as sealing them with resin, chromium trioxide, electroplating, and the penetration of Mn (Ref 4), to improve the properties of the coatings. The penetration of liquid Mn is effective for densifying the coating. In this study, the penetration treatment of ZrO_2 with Mn alloys, having lower liquidus and higher toughness that that of pure Mn, was carried out, and the densification and mechanical properties of the ZrO_2 coating were examined.

2. Materials and Experimental Procedure

The substrate was JIS SS400 (Japanese Standards Association, Tokyo, Japan) mild steel (15 by 15 by 3 mm); the surface was grit blasted before spraying. Commercially available ZrO_2 containing 8 wt% Y_2O_3 as a stabilizer (Shoden K-90, SHOWA DENKO Co., Ltd, Tokyo, Japan) was used as the feedstock. Particle size ranged from 10 to 44 μm. Plasma spraying was carried out in air, and yttria-stabilized zirconia (YSZ) coatings of 100 to 1000 μm thickness were produced. Mn alloy plates about 1 mm thick, consisting of 20, 40, 60, and 80 wt% Cu, 80 wt% Sn, and 70 wt% In, were used for the penetration treatment. Assemblies of the coatings and Mn alloys were ultrasonically degreased in acetone before heat treatment. The mechanical properties of the YSZ coatings heat treated with liquid Mn alloys were compared to sintered partially stabilized zirconia (PSZ) plates stabilized with 9.7 wt% Y_2O_3 (Nikato ZR6-Y, Nikato Co, Ltd, Osaka, Japan).

Keywords liquid manganese alloy, penetration, plasma-sprayed coating, sintering, zirconia

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Figure 1 shows a diagram of the experimental apparatus for the liquid Mn alloy penetration treatment. A YSZ (8 wt% Y_2O_3) tube with a 13 mm inside diameter and the Mn alloy were set on the surface of YSZ coatings. Mn alloy plates were placed in contact with the YSZ coating surface and then heated at 9.3×10^{-1} K/s in a vacuum of 1.33×10^{-3} Pa to a temperature that is 50 K higher than the liquidus line of the Mn alloys. After being held at this temperature, the assembly was cooled in the furnace at 2.5×10^{-2} K/s. Cross sections of as-sprayed YSZ coating and YSZ coating heat treated with liquid Mn alloys were examined by scanning electron microscopy (SEM). Changes in the elemental composition of the cross section of the coating were determined by electron probe microanalysis (EPMA). The fracture toughness of the coating before and after heat treatment with liquid Mn alloys and sintered Zr was obtained by the Niihara equation (Ref 5) using the indentation-fracture (IF) method, where the indentation load was 98 N for 20 s.

3. Results and Discussion

Plasma-sprayed ceramic coatings have a layered structure formed by the deposition of flattened, rapidly solidified parti-

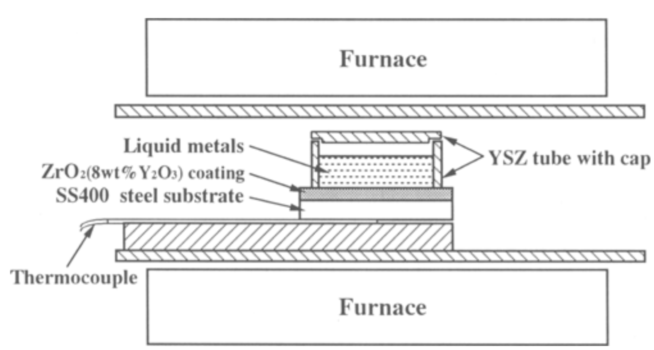

Fig. 1 Diagram of the experimental apparatus for liquid Mn alloy penetration treatment

cles. Connected porosity exists in as-sprayed coatings and consists of micropores, which are nonbonded areas between the ceramic lamellae and microcracks in individual flattened particles. Figure 2(a) shows a typical SEM microstructure of the YSZ coating. The diameters of these vertically and horizontally oriented porosities in the as-sprayed YSZ coating are about 0.3 to 0.5 μm and 0.17 to 0.3 μm, respectively. Figure 2(b) shows the microstructure of the fracture surface between layered particles in the coating. From the fracture surface, it was found that the bonded area ratio between layered particles in the coating is about 15%. Connected porosity exists in the as-sprayed coating. A three-dimensional diagram of the as-sprayed coating is shown in Fig. 2(c). The connected porosity from the coating surface to the interface between the coating and substrate is similar to the network shown in Fig. 2(c).

Table 1 shows the results of the penetration of Mn-Cu alloys. The apparent contact angles on the coating surface were measured by heating the alloys for 0.3 ks at various temperatures in a vacuum of 1.33×10^{-3} Pa. The liquid alloys with contact angles larger than 90° did not penetrate the coating while liquid alloys with smaller contact angles penetrated.

Figure 3 shows the images and surface analysis of Mn by EPMA for a coating cross section heat treated at 1473 K with Mn-20wt% Cu alloy for (a) and (b) 0.06 ks, (c) and (d) 1.8 ks, (e) and (f) 3.6 ks, and (g) and (h) 7.2 ks. In the case of 0.06 ks, liquid Mn-Cu alloy penetrated the coating from the surface to the

Table 1 Contact angles and penetration of various materials on YSZ coatings

Materials	Temperature, K	Contact angle, degree	Penetration
Cu	1408	155	None
Mn	1573	0	Penetrated
Mn-20Cu	1463	31	Penetrated
Mn-40Cu	1343	53	Penetrated
Mn-60Cu	1213	76	Penetrated
Mn-80Cu	1243	135	None

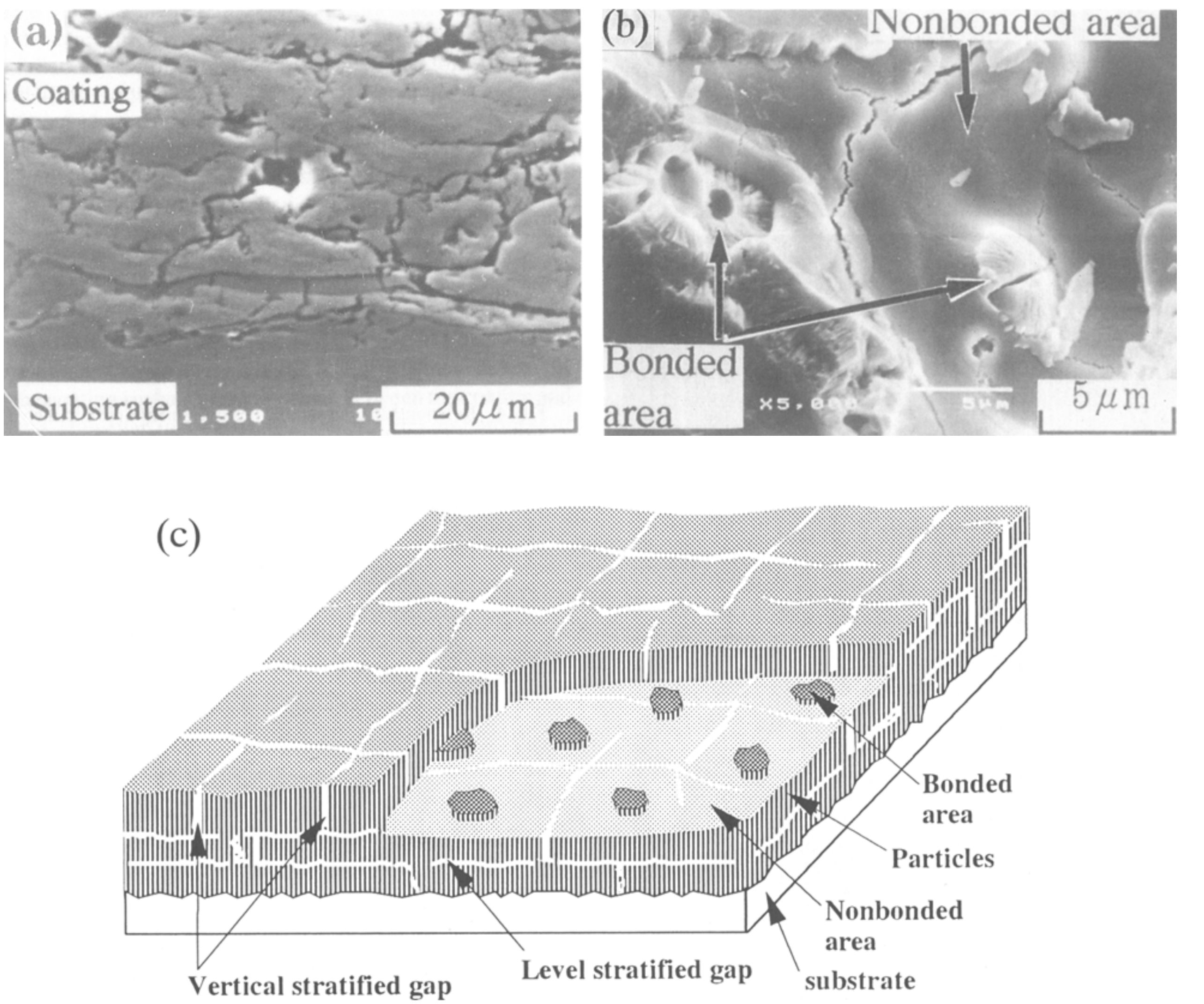

Fig. 2 (a) SEM images of the YSZ coating, (b) SEM images of fracture surface between YSZ layered particles, and (c) three-dimensional diagram of the YSZ coating and substrate

SS400 substrate. As heat treatment time increased, the concentration of Mn in the coating increased. These results show that the YSZ coating can change to a dense coating after heat treatment with liquid Mn-Cu alloy.

Table 2 shows the connected porosity for various coatings 100 μm thick. The connected porosity of coatings after heat

Table 2 Connected porosity for YSZ coatings with the thickness of 100 μm

Coatings	Connected porosity, %
As-sprayed YSZ coating	23.8
After heat treatment with Mn-20Cu; condition: 1463 K, 7.2 ks, 1.33×10^{-3} Pa	0
After heat treatment with Mn-40Cu; condition: 1343 K, 7.2 ks, 1.33×10^{-3} Pa	0
After heat treatment with Mn-60Cu; condition 1213 K, 7.2 ks, 1.33×10^{-3} Pa	0

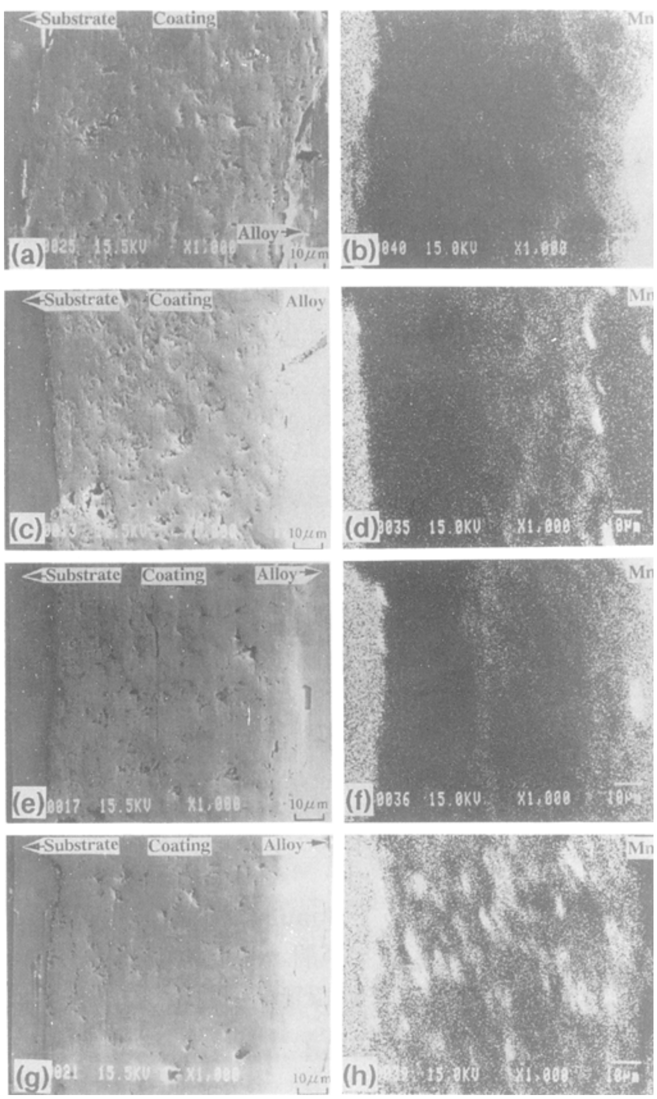

Fig. 3 SEM images and Mn surface analysis by EPMA for a cross section of YSZ coating heat treated at 1473 K with Mn-20wt% Cu alloy for (a) and (b) 0.06 ks, (c) and (d) 1.8 ks, (e) and (f) 3.6 ks, and (g) and (h) 7.2 ks

treatment with liquid Mn-Cu alloys was removed, and the coating was densified.

Figure 4 shows the relationship between the heat treatment time and the volume quantity of solid phase for coatings heat treated with liquid Mn-20Cu alloy at 1473 K in a vacuum of 1.33×10^{-3} Pa. The volume quantities were obtained by the equation:

$$V = S/(S + L + P) \times 100(\%) \qquad \text{(Eq 1)}$$

where V is the volume quantity, S is the YSZ phase area, L is the penetration phase of the liquid alloy area, and P is the porosity area.

The volume quantity of YSZ solid phase increases rapidly with treatment time to 1.8 ks and increases slowly after 1.8 ks. The volume quantity is approximately the same in the cases of 7.2 and 10.8 ks.

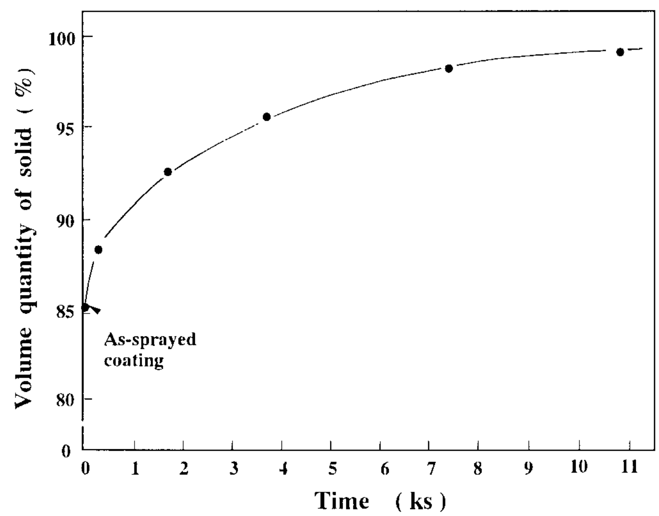

Fig. 4 Relationship between the heat treatment time and the volume quantity of YSZ solid phase

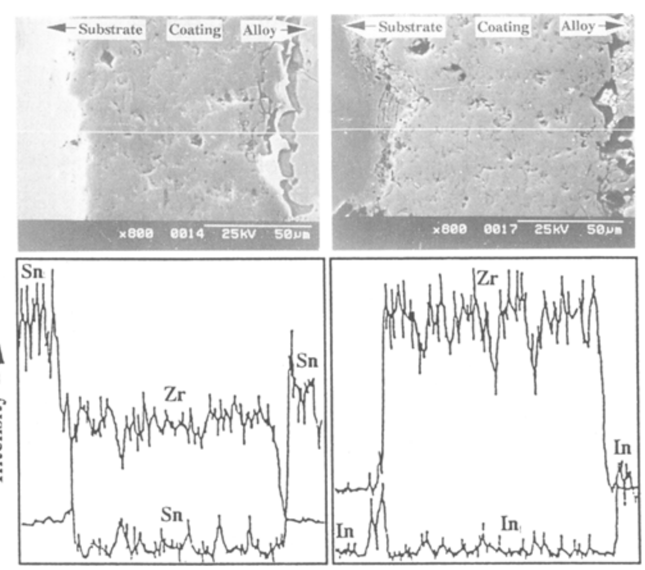

Fig. 5 SEM images and line analysis results of Zr, Sn, and In by EPMA for a cross section of YSZ coating heat treated with Mn-80Sn and Mn-70In at 1073 and 1273 K for 0.3 ks, respectively

Figure 5 shows the SEM images and line analysis results of Zr, Sn, and In obtained by EPMA for a cross section of the YSZ coating heat treated with Mn-80Sn and Mn-70In at 1073 and 1273 K for 0.3 ks in a vacuum of 1.33×10^{-3} Pa, respectively. Sn and In penetrated the YSZ coating to the substrate, and Sn diffused deeply into the steel substrate. The YSZ coating, heat treated with Mn-In and Mn-Sn, formed a dense coating compared to the as-sprayed coating.

Densification of the YSZ coating heat treated with liquid Mn alloys is mainly due to a sintering phenomenon that occurs by capillary pressure of liquid alloys penetrating microcracks in the coating. The capillary pressure of liquid Mn-Cu alloys of various composition acts as a driving force for liquid phase sintering and the following equation was obtained:

$$\Delta P = (4\, \gamma_{LV} \cos \theta)/d \qquad \text{(Eq 2)}$$

where ΔP is the capillary pressure, γ_{LV} is the surface energy of various liquid Mn-Cu alloys, θ is the contact angle of liquid alloy on YSZ coating, and d is diameter of the porosity.

Table 3 shows the capillary pressures obtained from Eq 2. From these results, the capillary pressures are calculated to be about 3.7 to 23.9 N/mm^2 and 2.2 to 13.6 N/mm^2 for 0.17 to 0.3 μm and 0.3 to 0.5 μm diameter porosity, respectively.

Figure 6 shows the Vickers hardness distribution of cross sections of YSZ coating after heat treatment with Mn-20Cu alloys for various heat treatment times. Results for the as-sprayed and sintered YSZ material are also given in Fig. 6. The average hardness of the YSZ coatings after heat treatment with Mn-20Cu increased with the heat treatment time, compared with about 740 HV for the as-sprayed YSZ coating. The hardness of a cross section of a coating heat treated with Mn-20Cu alloys for 7.2 ks reached about 1300 HV. In the case of 0.3 to 3.6 ks, the Vickers hardness of coating cross sections after heat treatment decreased from the coating surface to the interface between the coating and substrate. However, in the case of 7.2 ks, the Vickers hardness of coating cross sections after heat treatment was approximately uniform. These results show that the increase of Vickers hardness of the YSZ coating with Mn-Cu alloys depends mainly on a degree of densification of the coating, which is brought out by liquid phase sintering of Mn-Cu alloys. Moreover, the Vickers hardness of the YSZ coating heat treated with Mn-70Sn alloy for 7.2 ks was about 950 HV and was lower than that of YSZ coating heat treated with Mn-20Cu alloy. The YSZ coating heat treated with Mn-70Sn alloy was not as dense as the coating heat treated with Mn-20Cu alloy.

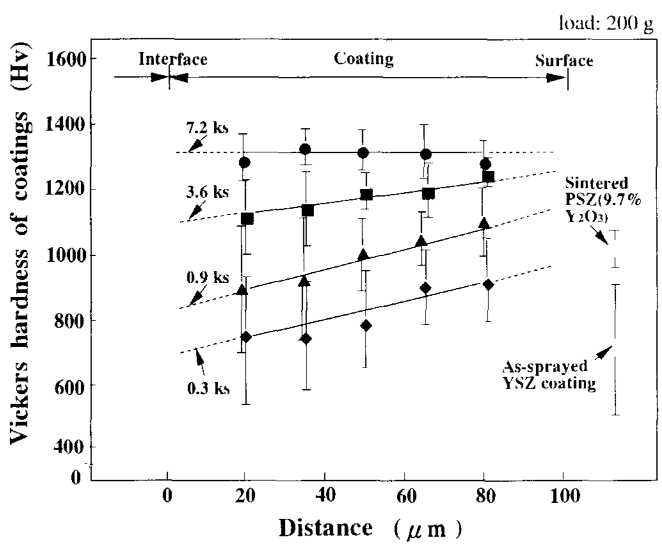

Fig. 6 Vickers hardness distribution of cross sections of YSZ coating after heat treatment with Mn-20Cu alloys for various heat treatment times

The fracture toughness of the coating heat treated with Mn-Cu alloy was measured by the IF method and compared with sintered PSZ. The fracture toughness can be obtained as follows:

$$K_c = 0.203\,(C/a)^{-3/2} \cdot H \cdot a^{1/2} \qquad \text{(Eq 3)}$$

$$H = 1.8544P/(2a)^2 \qquad \text{(Eq 4)}$$

where K_c is the fracture toughness, H is the Vickers hardness, P is the indentation load, C is the half average crack length, and a is half the average length of the diagonal line of indentation.

The occurrence of median cracks and $C/a > 2.5$ was observed in the samples. Figure 7 shows the results for coatings heat treated with Mn-20Cu, Mn-40Cu, Mn-60Cu, sintered PSZ (9.7 wt% Y_2O_3), and as-sprayed YSZ coating. The fracture toughness of YSZ coating after heat treatment with Mn-Cu alloy increased as the content of Cu increased. The fracture toughness

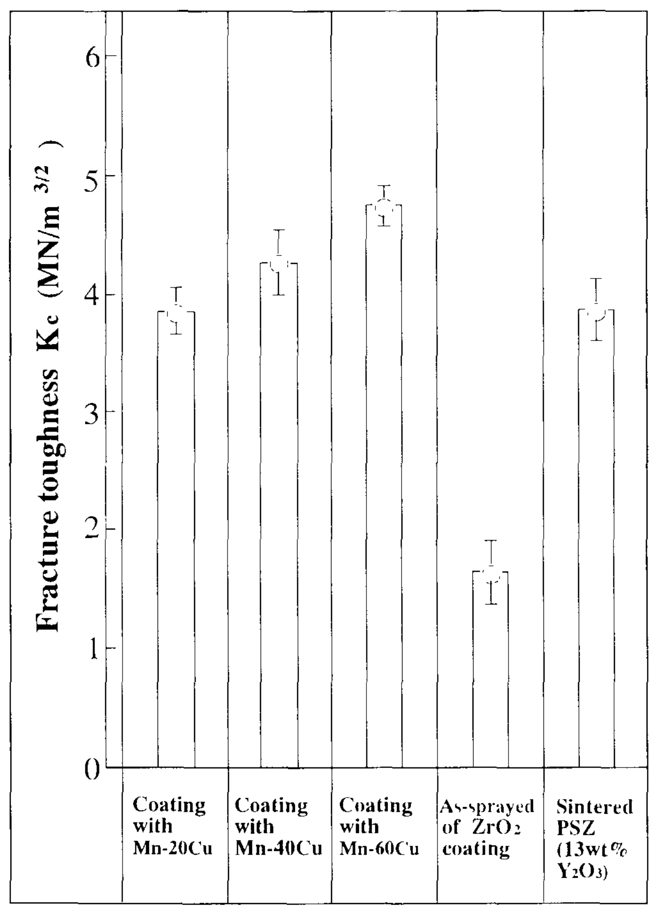

Fig. 7 Fracture toughness measured for YSZ coating heat treated with Mn-20Cu, Mn-40Cu, Mn-60Cu, sintered PSZ (9 7 wt% Y_2O_3), and as-sprayed YSZ coating

Table 3 Capillary pressure in YSZ coatings and surface energy of Mn-Cu alloys

Materials	ΔP, N/mm^2 d = 0.17 μm	d = 0.3 μm	d = 0.5 μm	γ_{LV}, J/m^2	Measure temperature, K	Contact angle, degree
Mn-20Cu	23.91	13.55	8 13	1.1121	1473	24
Mn-40Cu	20.71	11.74	7 04	1 1170	1473	38
Mn-60Cu	6 53	3.70	2 22	1.1473	1473	76

of coating heat treated with Mn-20Cu, Mn-40Cu, and Mn-60Cu reached about 3.9, 4.3, and 4.7 MN/m$^{3/2}$, respectively. It was recognized that the fracture toughness of coating heat treated with Mn-Cu alloys increased greatly compared with the as-sprayed coating to a value of about 3.8 MN/m$^{3/2}$, which was similar to the fracture toughness of sintered PSZ (13 wt% Y_2O_3). The increase of fracture toughness of the coating heat treated with Mn-Cu alloy is due to the increase of toughness of the Mn-Cu alloy phase, which increases with the content of Cu in the YSZ coating.

4. Conclusions

In this study, the liquid Mn alloy penetration treatment for plasma-sprayed YSZ coating was carried out by heating in a vacuum atmosphere to improve the mechanical properties of porous YSZ coatings. The main results include the following.

- The penetration of liquid Mn-Cu alloys in YSZ coatings was observed for alloys over 40 wt% Mn content by heating in a vacuum of 1.33×10^{-3} Pa.
- The mechanical properties of YSZ coating after heat treatment with Mn alloys were improved by liquid phase sintering, compared with the as-sprayed YSZ coating. The Vickers hardness and fracture toughness of YSZ coating heat treated with Mn-20wt%Cu alloys was about 1300 HV and 4.7 MN/m$^{3/2}$, respectively.

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