Influence of Pores on Wettability of Zirconia Ceramic by Molten Manganese

著者	Shinozaki Nobuya, Kaku Hiroshi, Mukai Kusuhiro
journal or publication title	Transactions of JWRI
volume	30
number	Special Issue
page range	161-166
year	2001-07
URL	http://hdl.handle.net/10228/00006421

INFLUENCE OF PORES ON WETTABILITY OF ZIRCONIA CERAMIC BY MOLTEN MANGANESE

Nobuya SHINOZAKI, Hiroshi KAKU, and Kusuhiro MUKAI
Kyushu Institute of Technology, Sensui-cho, Tobata, Kitakyushu, 804-8550, JAPAN

ABSTRACT

A basic research study for improvement of plasma-sprayed zirconia coatings has been conducted. Wettability of porous ZrO_2-Y_2O_3-MnO substrates by manganese has been investigated at 1573K by the sessile drop method. The contact angles tend to decrease gradually and stabilized at 85-90 degrees. Those values are larger than that for dense substrate. Thus the pores have a great influence on kinetics of wetting.

INTRODUCTION

The plasma spraying of ceramic powder is one of the methods to improve the surface properties of metallic materials used under a severe environment. However, owing to a lot of pore existing in as-sprayed coating, the performance of the film, for instance, oxidation resistance, corrosion-resistance, and mechanical strength at high temperature, is not enough. Infiltrating a molten metal can eliminate the pores; a manganese alloy has been considered as the metal [1].

Because the infiltration depends on capillarity, it is important to know the surface tension of the molten metal and the contact angle between the molten metal and the ceramic. The contact angle of molten manganese on zirconia ceramics was found by the authors to be about 80 degrees or less [2]. The research has been continued further, and the wettability of zirconia substrate having porous surface by molten manganese is reported at this time.

EXPERIMENTS

1. Materials

Figure 1 shows how to make dense and porous substrates.

The transfer of manganese from a manganese droplet to a ZrO_2-5.1mass%(3mol%)Y_2O_3 substrate was confirmed in the previous study: the manganese concentration at substrate

Nobuya SHINOZAKI, Sensui-cho, Tobata, Kitakyushu, 804-8550, JAPAN, Fax 093-884-3364

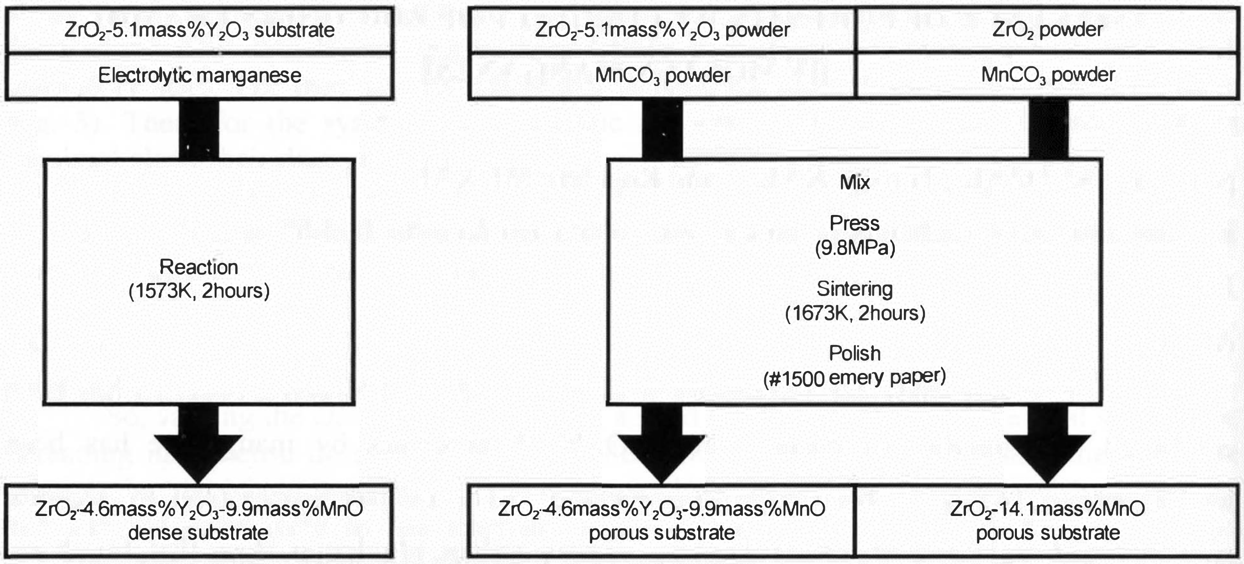

Figure 1 Making procedure of substrate.

surface after reaction for 1-3 hours at 1573K was 7.7mass%[2]. Referring to the research of Dravid [3], it has been guessed that manganese exists in the substrate as MnO. Therefore, contacting commercial ZrO_2-5.1mass% Y_2O_3 substrates with molten manganese for one hour at 1573K made ZrO_2-Y_2O_3-MnO substrates with dense surfaces.

ZrO_2-5.1mass%Y_2O_3 powder of 99.5% purity and $MnCO_3$ powder of 99% purity were mixed, pressed, and the compact was sintered for two hours at 1673K in argon gas. $MnCO_3$ was decomposed by heating to remain as MnO. The amount of $MnCO_3$ was adjusted so that the MnO concentration of substrate might become 9.9mass%, which corresponds to 7.7mass% manganese. Many pores exist in the substrates made by this method.

Because according to Dravid [3] the zirconia particle can contain 14.1mass% MnO, the ZrO_2-14.1mass%MnO substrates were also made from 99.5% pure ZrO_2 powder and 99% pure $MnCO_3$ powder by sintering for two hours at 1673K in argon gas. Many pores exist in the substrates as well as in the ZrO_2-Y_2O_3-9.9mass%MnO substrate.

These three different substrates containing MnO were made in order to reduce the influence of reaction between molten manganese and substrate on measurements of wetting. All the substrates consist of cubic zirconia particles, and were used in experiments after polishing by #1500 emery paper.

Electrolytic manganese of 99.9mass% purity was processed as hexagonal plates of 0.4g with 1mm in thickness. Before the experiment the surfaces of plates were polished.

2. Experimental procedure

A schematic view of the apparatus used in experiments is shown in Figure 2.

At first, several manganese plates were piled on zirconia substrate and they were set in a

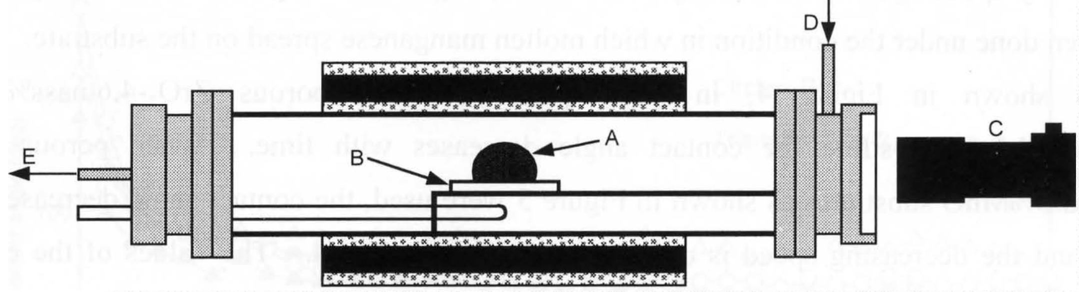

Figure 2 Schematic view of experimental apparatus.

reaction tube made of alumina.. The tube was evacuated and then argon gas was supplied. Argon gas was supplied continuously during a run. Zirconia substrate and manganese samples were heated at the rate of 500K/h and were maintained at1573K for up to 3 hours. Pictures of molten manganese were taken at intervals of 5min at 1573K, and the contact angles between substrate and molten manganese were measured (by using computer) with error less than ±0.5%. Further details on measurements have been reported in the previous paper [2].

RESULTS

The surface condition of these three kinds of substrates is shown in Figure 3. As seen in Figure 3a, the ZrO_2-Y_2O_3-MnO reaction layer formed on the surface of ZrO_2-5.1mass%Y_2O_3 substrate by reaction with molten manganese is very dense. On the other hand, many pores exist in ZrO_2-4.6mass%Y_2O_3-9.9mass%MnO substrate and ZrO_2-14.1mass%MnO substrate made from the powders: the amount and the size of pores of both substrates are similar (refer to Figure 3b, and c).

Examples of the contact angle are shown in Figure 4. The horizontal axis shows the holding time after reaching the temperature of measurement. In the experiment using substrate with a dense surface, the contact angle is steady during the measurement. The values are in good agreement at both sides of droplet. The average contact angle of this experiment is 78deg, and it almost agrees with that has already been obtained by using the commercial substrates of ZrO_2-5.1mass%Y_2O_3 substrate and ZrO_2-13.5mass%Y_2O_3.

Strictly speaking, the contact angle is an advancing contact angle because the experiment has been done under the condition in which molten manganese spread on the substrate.

As shown in Figure 4, in the experiment using porous ZrO_2-4.6mass%Y_2O_3-9.9mass%MnO substrate the contact angle decreases with time. When porous ZrO_2-14.1mass%MnO substrates as shown in Figure 5 were used, the contact angle decreases with time, and the decreasing speed is different in each experiment. The values of the contact angle are different at the right and the left sides of droplet and occasionally keep decreasing three hours later. The contact angle seems to be finally steady to 85-90 deg. It becomes evident from these results that pores have exerted some influences on wetting kinetics.

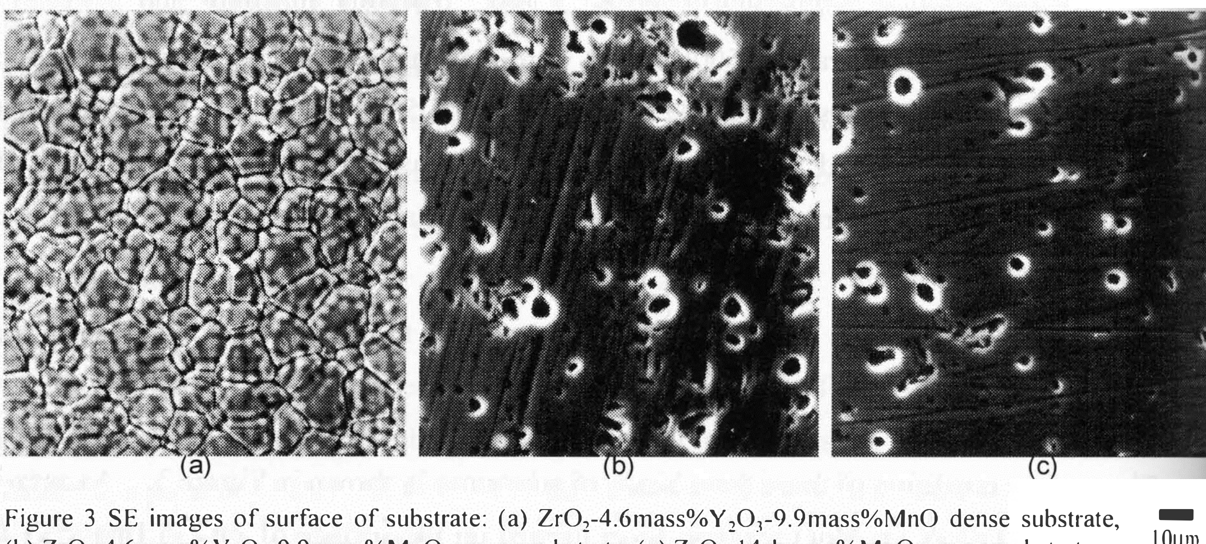

Figure 3 SE images of surface of substrate: (a) ZrO_2-4.6mass%Y_2O_3-9.9mass%MnO dense substrate, (b) ZrO_2-4.6mass%Y_2O_3-9.9mass%MnO porous substrate, (c) ZrO_2-14.1mass%MnO porous substrate.

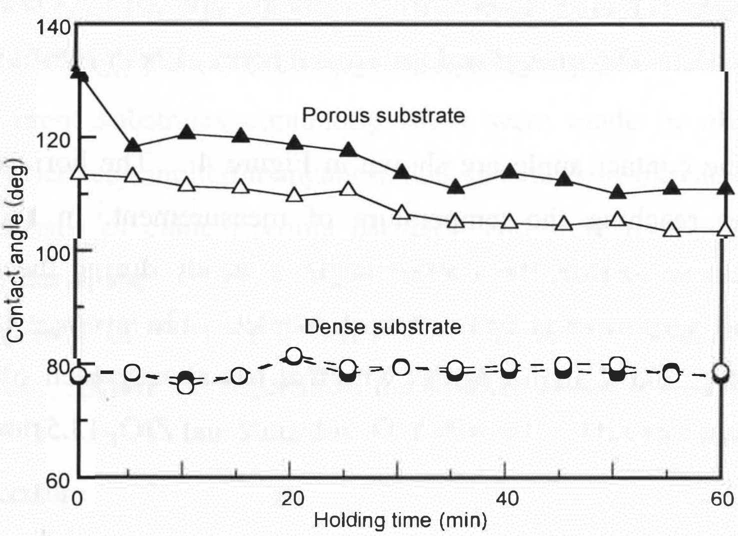

Figure 4 Contact angle obtained when dense and porous ZrO_2-4.6mass%Y_2O_3-9.9mass%MnO substrate were used at 1573K: ○ and △ are from the left side, and ● and ▲ are from the right side of droplet.

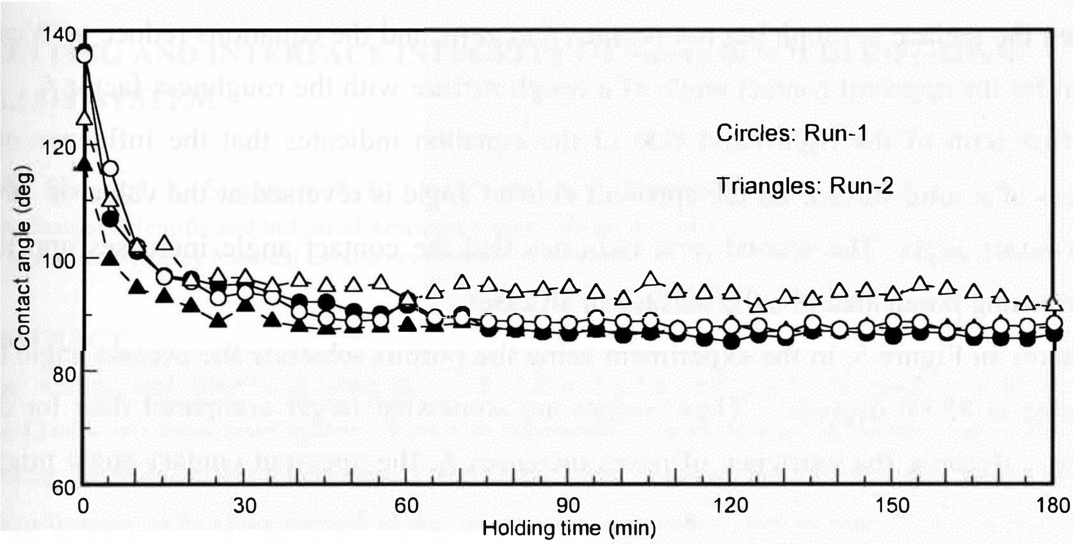

Figure 5 Contact angle obtained in two experiments where ZrO_2-14.1mass%MnO porous substrates were used at 1573K: ○ and △ are from the left side, and ● and ▲ are from the right side of droplet.

DISCUSSION

It is often said that the chemical reaction at solid-liquid interface influences wetting, and decreases the contact angle. In this study we used a substrate with ZrO_2-Y_2O_3-MnO layer on its surface to suppress the reaction with manganese. Then as described above, the contact angle is 78deg, and is comparable to those obtained previously using the ZrO_2-5.1mass%Y_2O_3 substrate [2]. It can be concluded from this result that the molten manganese and dense ZrO_2-Y_2O_3-MnO system gets wet even if an intense interfacial reaction does not take place.

As mentioned above, the existence of pores brings a big difference to the change of the contact angle with time. Moreover, a long time is necessary until the contact angle reaches a constant value. The reason is probably that an increase of the free energy occurs when molten manganese spreads over the pores and disturbs the spreading.

Wenzel [4] has suggested that the contact angle is influenced by the roughness of solid surface. Cassie and Baxter [5] have extended their analysis to porous surfaces.

The change in the interface free energy when a liquid spread over a unit area of a porous solid surface is examined, and the next equation is can be derived.

$$\cos\theta_A = f_1 \cos\theta - f_2 \tag{1}$$

θ_A, θ, f_1, and f_2 are the apparent contact angle, the contact angle for a smooth solid surface, the total area of solid-liquid interface, and the total area of liquid-air interface on a plane geometrical surface of unity area parallel to the rough surface, respectively.

When the surface is rough but not porous, f_2 is zero, and the equations reduce to Wenzel's equation for the apparent contact angle of a rough surface with the roughness factor f_1. That is, the first term of the right hand side of the equation indicates that the influence of the roughness of a solid surface on the apparent contact angle is reversed at the value of 90deg of the contact angle. The second term indicates that the contact angle increases apparently with increasing pored area of solid surface in all cases.

As show in Figure 5, in the experiment using the porous substrate the contact angle tends to stabilize at 85-90 degrees. These values are somewhat larger compared than for dense substrate. Because the existence of pores increases f_2, the apparent contact angle might be larger.

In the future, the influence of pores on the wettability might be clarified by further examination using the substrate in different porosity.

COCLUSIONS

The wettability of porous ZrO_2-Y_2O_3-MnO substrates by molten manganese was investigated at 1573K under Ar. Some differences were observed in comparison with the wetting on dense substrates.

The contact angle decreased gradually and a long time was necessary until it reached a constant value. The values of contact angles at the right and the left of manganese droplet were different. The contact angles decreased finally up to 85-90 degrees: those values were larger than that obtained for dense substrates.

Generally, it has been found that the pores greatly influence kinetics of wetting.

REFERENCES

1. Z. Zhou, A. Ohmori, K. Inoue, and K. Murakami, J. High Temperature Soc., Vol.20, pp.301-309, (1994).

2. N. Shinozaki, M. Sonoda, and K. Mukai, Met. Trans., Vol.29A, pp.1121-1125, (1998).

3. V. P. Dravid, V. Ravikumar, M. R. Notis, C. E. Lyman, G. Dhalenne, and A. Revcolevschi, J. Am. Ceram. Soc., Vol.77, pp.2758-2762, (1994).

4. R. N. Wenzel, Ing. Eng. Chem., Vol.28, p.988, (1936).

5. A. B. D. Cassie and S. Baxter, Trans. Farady Soc., Vol.40, pp.546-551, (1944).