

# Influence of Pores on Wetting of Alumina- and Zirconia-base Ceramics

## by Molten Manganese

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Most of the wetting systems between ceramics and metals are accompanied by interfacial reactions. These interfacial reactions make the wetting phenomena complicated<sup>[1]</sup>. For instance, Aksay et al.<sup>[2]</sup> explained the transient minimum of contact angle in connection with the free energy of reaction. Nakae et al.<sup>[1]</sup> showed that the wetting progressed through four steps: dynamic non-equilibrium step, quasi-equilibrium step, chemical non-equilibrium step and equilibrium step. Besides those influence of reaction itself on wetting, the

workers have to pay attention to the change of geometrical condition of interface. In this study, the authors investigated an influence of pores existing in interface on wetting under the assumption that pores would be produced in a reaction layer. Manganese metal, alumina ceramic and zirconia ceramic were chosen as starting materials. Manganese is expected to form a stable oxide of  $\text{MnAl}_2\text{O}_4$  spinel phase, reacting with alumina<sup>[3]</sup> and diffuses into zirconia in accordance with oxygen to change to a stable phase of cubic zirconia<sup>[4,5]</sup>.

Contact angle was measured by means of the sessile drop method where the metallic manganese and ceramic substrate were held at a high temperature of 1573K in argon atmosphere.

In order to change the substrate surface condition, two types of alumina-base substrates were prepared. Firstly, molten manganese was kept on alumina substrate at a higher temperature of 1773K for 1 hr followed by furnace cooling. The solidified manganese was removed from the substrate at room temperature, resulting in the dense substrate with only a few pores as shown in Figure 1a. The surface was smooth as well as an alumina substrate before heating: the surface roughness  $R_a$  was in a range from 0.3 to 0.6 $\mu\text{m}$ . The substrate surface was confirmed to be of  $\text{MnAl}_2\text{O}_4$  spinel phase using X-ray diffraction technique. Next, porous  $\text{MnAl}_2\text{O}_4$  spinel substrate was prepared in

an another way where alumina and manganese carbonate powders were mixed, pressed, sintered at 1673K for 2 hrs and polished with #1500 emery paper. There exist many pores as shown in Figure 1b and its apparent porosity fraction,  $p$ , was measured to be 0.43 using the Archimedes method. The surface roughness was measured for the reference although surface roughness measuring device is unsuitable for porous materials. Owing to the pores,  $R_a$  was high value of  $1.4\mu\text{m}$ .

Also two types of zirconia-base substrates were prepared. Dense  $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-MnO}$  substrate was prepared in the same procedure for making dense  $\text{MnAl}_2\text{O}_4$  substrate, in which  $\text{ZrO}_2\text{-3mol\%(5.1mass\%)\text{Y}_2\text{O}_3}$  substrate and molten manganese were reacted. Figure 2a shows a scanning electron (SE) micrograph of the surface with no pore. Manganese concentration was 7.7mass%, i.e. 9.9mass% as MnO, in a region near to the free surface. The substrate surface was smooth and the surface roughness  $R_a$  was in a range from 0.1 to  $0.2\mu\text{m}$ . Another type of porous  $\text{ZrO}_2\text{-4.6mass\%Y}_2\text{O}_3\text{-9.9mass\%MnO}$  substrate was made from  $\text{ZrO}_2\text{-5.1mass\%Y}_2\text{O}_3$  and manganese carbonate powders: those powders were mixed and sintered at 1673K for 2 hrs followed by polishing with #1500 emery paper. There exist pores in the size of 1 to  $5\mu\text{m}$  as shown in Figure 2b and its apparent porosity fraction,  $p$ , is 0.10. The surface roughness  $R_a$  was

0.3 $\mu\text{m}$ , slightly higher than that of the dense substrate. These zirconia-base substrates consisted of cubic phase.

Several thin plates of electrolytic manganese were piled up high on the substrate before heating as shown in Figure 3a. The manganese plates were molten by heating and the molten manganese spread over the substrate. A photograph of manganese droplet immediately after melting is shown in Figure 3b: the contact angle between molten manganese and substrate was high about 120deg for any substrate prepared here. It took several minutes to reach the measurement temperature of 1573K after melting of manganese.

Figure 4 shows contact angles measured at 1573K using the two types of  $\text{MnAl}_2\text{O}_4$  spinel substrates. There is an apparent difference in contact angle depending on the surface condition and the contact angle shows high values when the substrate has a large amount of porosity. The  $\text{MnAl}_2\text{O}_4$  spinel substrate having a little pore was further densified after the experiment, resulting in a surface with no pore and larger grains of 5 to 10  $\mu\text{m}$ . On the other hand, the surface conditions of porous  $\text{MnAl}_2\text{O}_4$  substrates before and after the measurement were similar one another.

Figure 5 shows contact angles for  $\text{ZrO}_2$ -4.6mass% $\text{Y}_2\text{O}_3$ -9.9mass%MnO substrates. The contact angle for the dense substrate is constant being about 79

deg although it slightly decreases in an early stage of measurement. For the porous substrate, it took 2 hrs until the contact angle reaches constant value and the angle is higher than that for the dense substrate. The change in the contact angle during experiment is not due to the interfacial reaction and the change in geometrical condition of interface because the composition and the geometry of substrate surface have hardly changed before and after experiment at all. The slow spreading of manganese is provably due to disturbance of pores. The reason seems to be that a considerable increase in free energy is required to make newly up manganese-pore interface when molten the manganese spreads over the porous substrate.

Wenzel <sup>[6]</sup> has proposed the following equation for the wetting of rough surface as shown in Figure 6a:

$$\cos \theta_A = r \cos \theta \quad (1)$$

Here  $\theta_A$  and  $\theta$  are the apparent contact angle for rough surface, and the contact angle for smooth surface, respectively. The roughness factor  $r$  is the ratio of actual surface to geometrical surface. Equation (1) means that the contact angle decreases apparently with increasing surface roughness when  $\theta$  is less than 90deg. It is evident, therefore, that Wenzel's consideration cannot explain the present results. The reason seems to be because there is non-wetted area in the

substrate surface. It has already been confirmed that molten manganese could not penetrate into pores of  $\text{MnAl}_2\text{O}_4$  substrate [3].

Cassie and Baxter [7] have extended Wenzel's consideration [6] to the wetting of porous surface as shown in Figure 6b and presented the following equation:

$$\cos \theta_A = f_1 \cos \theta - f_2 \quad (2)$$

Here,  $f_1$  and  $f_2$  are the total area of solid-liquid interface and the total area of liquid-gas interface on a plane geometrical surface of unity area parallel to the rough surface, respectively.

The interface between molten manganese and porous substrate is supposed to be like shown in Figure 7a. Although the factors  $f_1$  and  $f_2$  are influenced by the surface roughness, it is impossible to estimate accurately those factors from  $R_a$  value. Then, assuming the simple interface as shown in Figure 7b, equation (2) was applied to the present investigation to estimate the apparent contact angle for the porous substrates. Here,  $f_1$  and  $f_2$  can be estimated easily on the basis of the porosity of substrate surface, that is,  $f_1 = 1-p$  and  $f_2 = p$ . Owing to this simplification, equation (2) means that the apparent contact angle increases with increasing porosity of substrate. The contact angles for smooth solid surface,  $\theta$ , are 87 deg for  $\text{MnAl}_2\text{O}_4$  spinel and 79 deg for

ZrO<sub>2</sub>-4.6mass%Y<sub>2</sub>O<sub>3</sub>-9.9mass%MnO (see Figures 4 and 5). Substituting these values for  $\theta$  in equation (2), the apparent contact angles,  $\theta_A$ , are calculated to be 114 deg for MnAl<sub>2</sub>O<sub>4</sub> spinel with porosity of 0.43 and 86deg for ZrO<sub>2</sub>-4.6mass%Y<sub>2</sub>O<sub>3</sub>-9.9mass%MnO with porosity of 0.10. These contact angles are in good agreement with those measured as shown in Figures 4 and 5.

The present study indicates that the pores influence on wetting provided the pores are produced by any reaction at the metal-ceramic interface, that is, the presence of pores increases the contact angle. Given high porosity, wettable metal-ceramic system changes provably to non-wettable system. In other words, we can control the wetting of metal-ceramic well by controlling the porosity of ceramic. This way of thinking is provably useful even in the field of metal casting because the wetting between molten metal and mold plays an important role in casting processes. The authors are further studying on the wetting using ceramic substrates with various porosities in order to clarify the influence of pores on metal-ceramic wetting.

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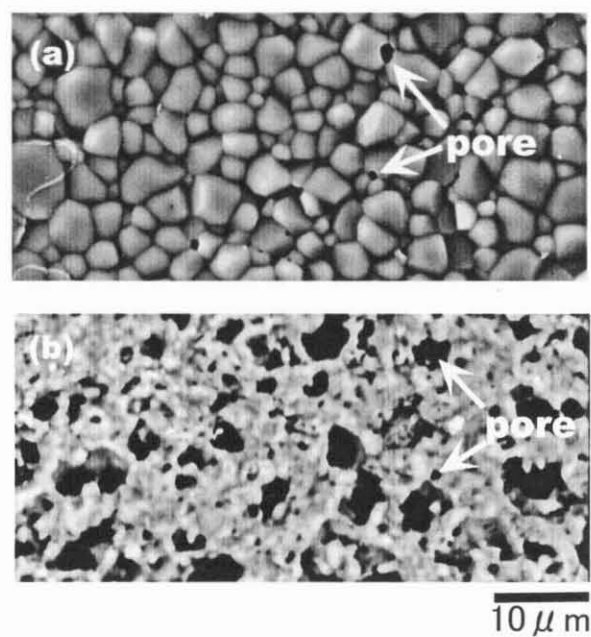


Fig.1 SE images of surfaces of MnAl<sub>2</sub>O<sub>4</sub> spinel substrates: a, dense substrate produced by manganese-alumina heated for one hour at 1773 K; b, porous substrate sintered at 1673 K for 2 hrs.

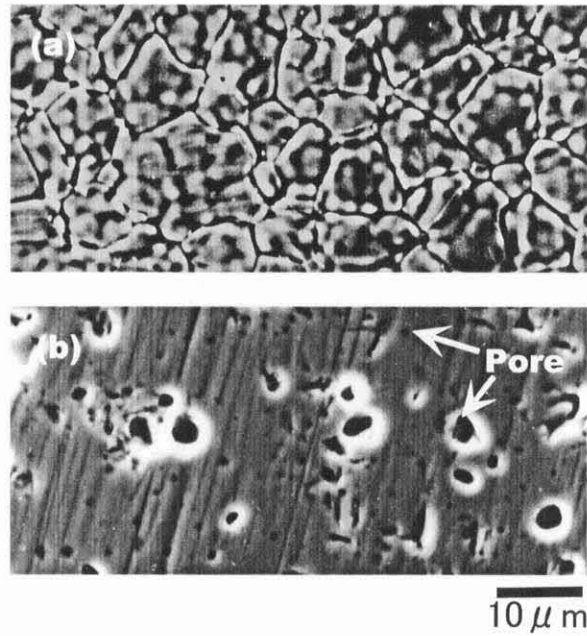


Fig.2 SE images of surfaces of  $\text{ZrO}_2$ -4.6mass% $\text{Y}_2\text{O}_3$ -9.9mass%MnO substrates: a, dense substrate produced by manganese-zirconia(yttria) heated for one hour at 1773 K; b, porous substrate sintered at 1673 K for 2 hrs.

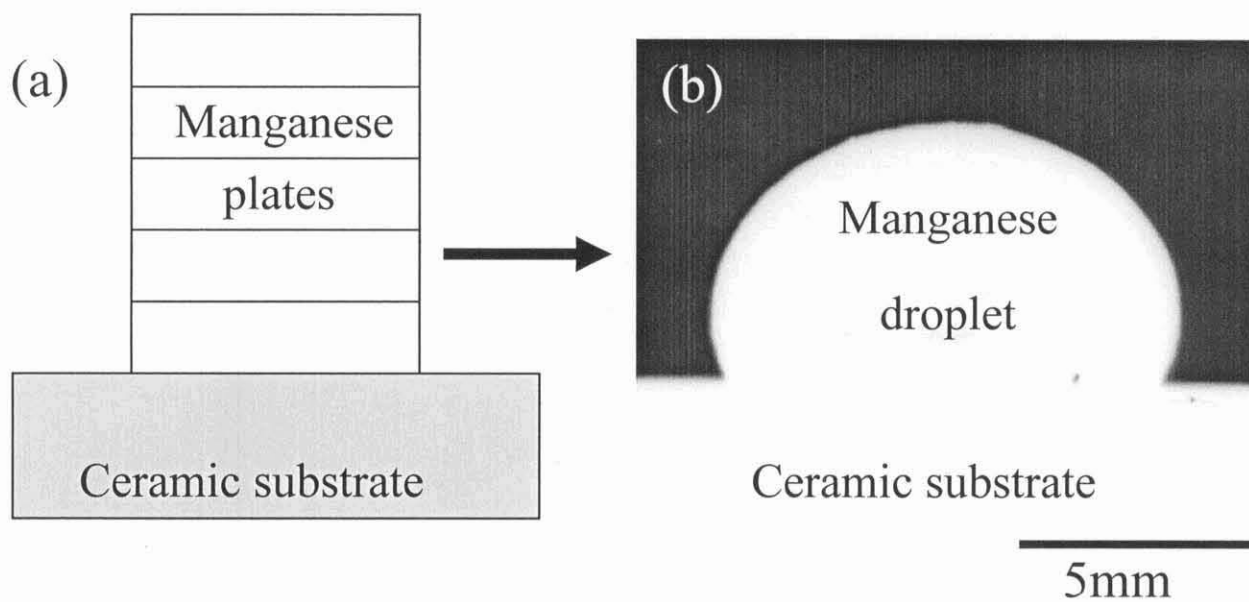


Fig.3 Manganese on substrate: a, manganese plates piled up on substrate before heating; b, photograph of manganese droplet immediately after melting.

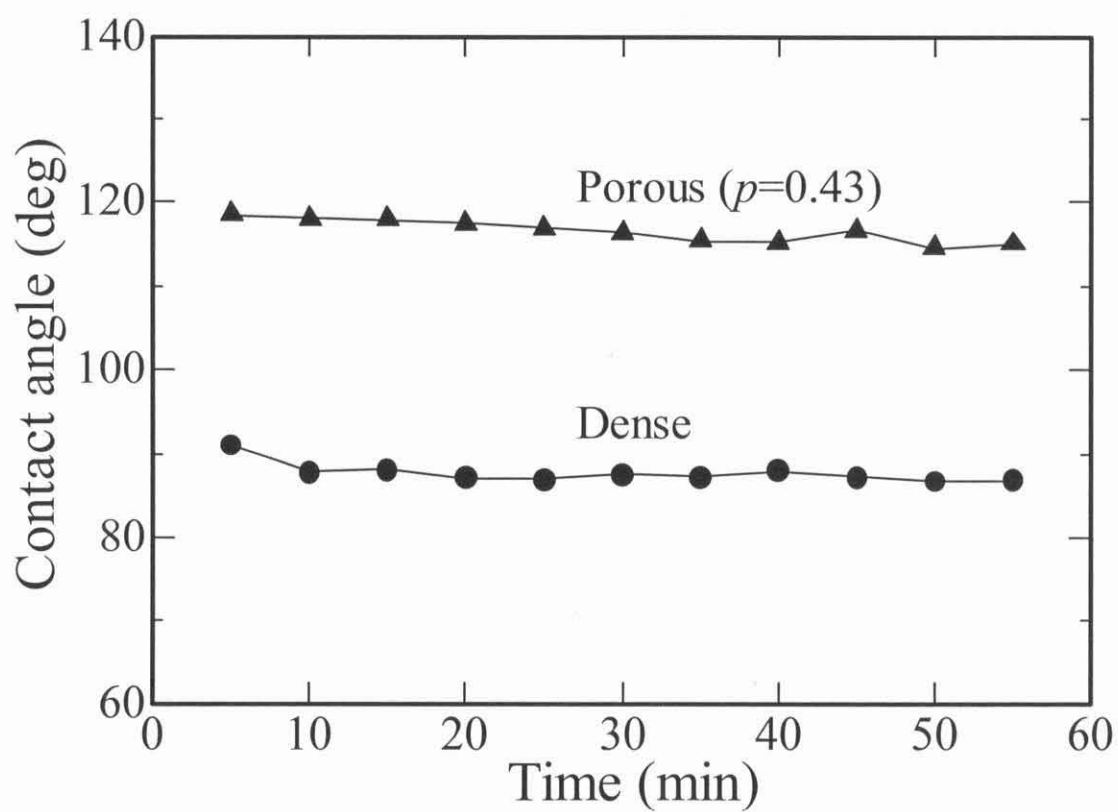


Fig.4 Change in contact angle as a function of measuring time for two-types of  $\text{MnAl}_2\text{O}_4$  spinel substrates measured at 1573K.

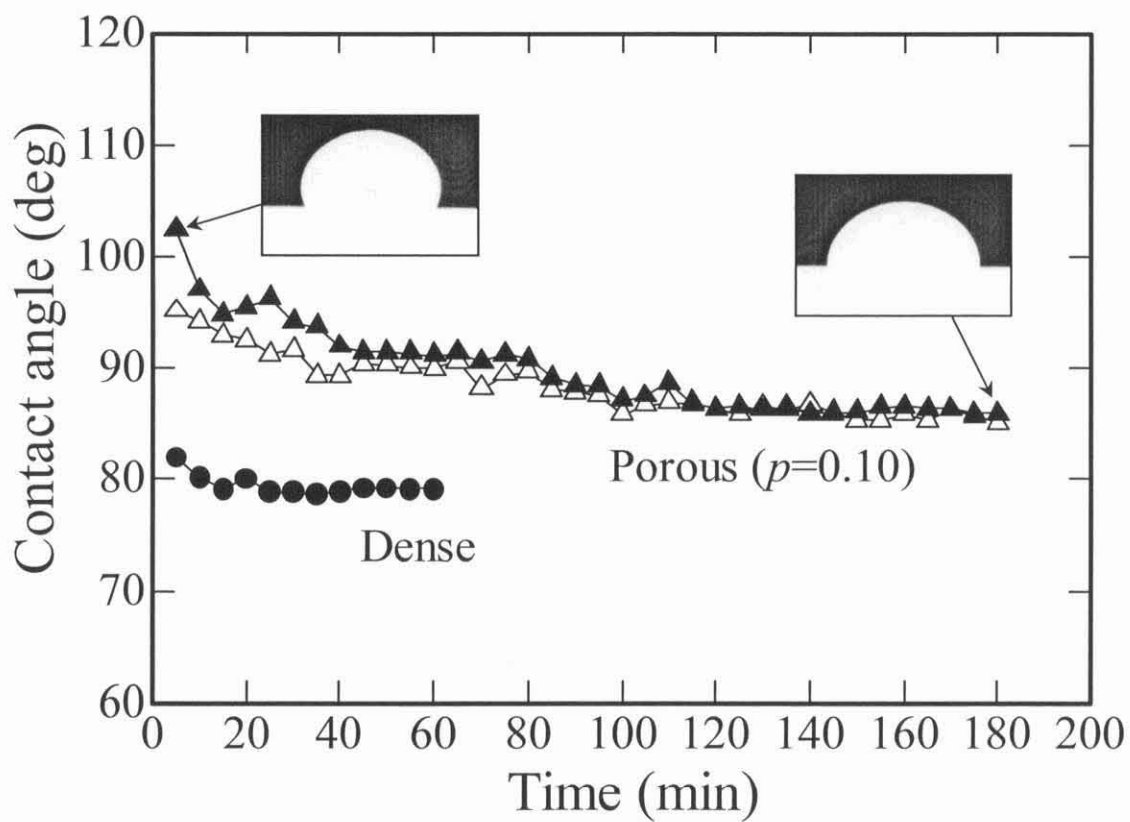


Fig.5 Change in contact angle as a function of measuring time for two-types of  $\text{ZrO}_2$ -4.6mass% $\text{Y}_2\text{O}_3$ -9.9mass%MnO substrates measured at 1573K.

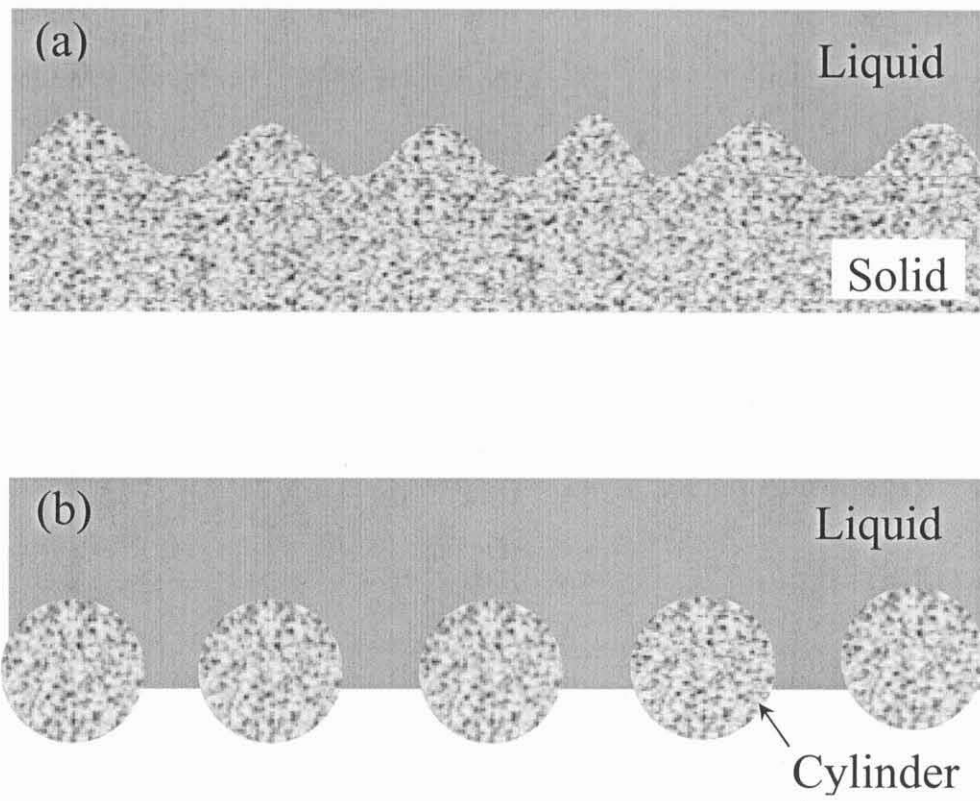


Fig.6 Two interfacial models: a, Wenzel's model for rough surface<sup>[6]</sup>; b, Cassie and Baxter's model for porous surface<sup>[7]</sup>.

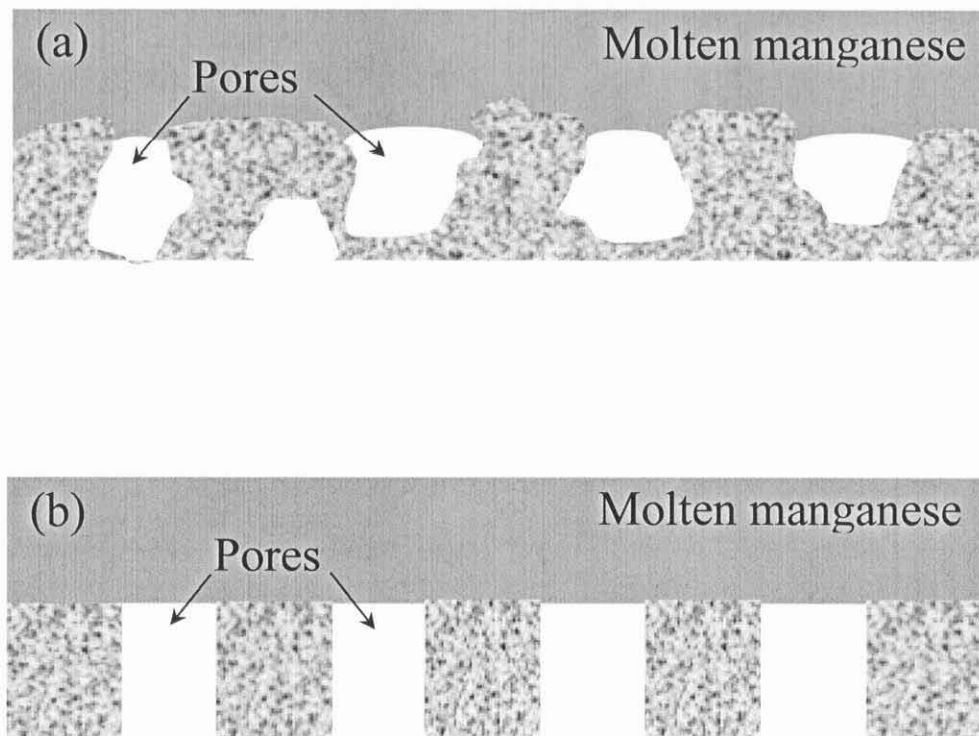


Fig.7 Simplification of porous interface in order to estimate apparent contact angle on the basis of Cassie and Baxter's equation<sup>[7]</sup>: a, molten manganese-porous substrate interface; b, simplified model for porous interface.