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Wetting Phenomena at High Temperature (Part II)[†]

Kiyoshi NOGI*, Nobuya IWAMOTO** and Kazumi OGINO***

Abstract

Wetting phenomena in the deoxidation process of liquid steel was described in the previous review (see Part I). It was clarified that we have to control the wettability of inclusions by liquid steel to obtain clean steel.

In the present review, we will discuss factors affecting the wettability of solid.

KEY WORDS :(Wettability) (Deoxidation) (Surface Tension) (Contact Angle) (Joining)

4.2 Factors affecting the wettability

Factors affecting the wettability of ceramics by liquid metal can be summarized as follows;

1. thermodynamical stability of ceramics and metals
2. temperature
3. atmosphere (especially oxygen potential)
4. surface characteristics of ceramics (surface roughness and crystal orientation)
5. alloying element and impurity

We will discuss here the effect of above each factor on the wettability of ceramics by liquid metals.

4.2.1 Thermodynamical stability of ceramics and metals

Naidich¹⁾ and McDonald et al²⁾ reported that the

wettability of solid oxide by liquid metal is effected by thermodynamical stability of oxide and metal.

Naidich found that contact angles of liquid metal / solid oxide systems closely relate to a difference in free energy changes between with the oxidizing reaction of the liquid metals and with the dissociation reaction of solid oxides.

On the other hand, McDonald clarified that the more negative in free energy change of oxide formation from metal, the larger the work of adhesion between liquid metal and alumina.

Two of authors revealed a relationship between surface free energy change(work of adhesion per mole) and free energy change of oxide formation in liquid metal

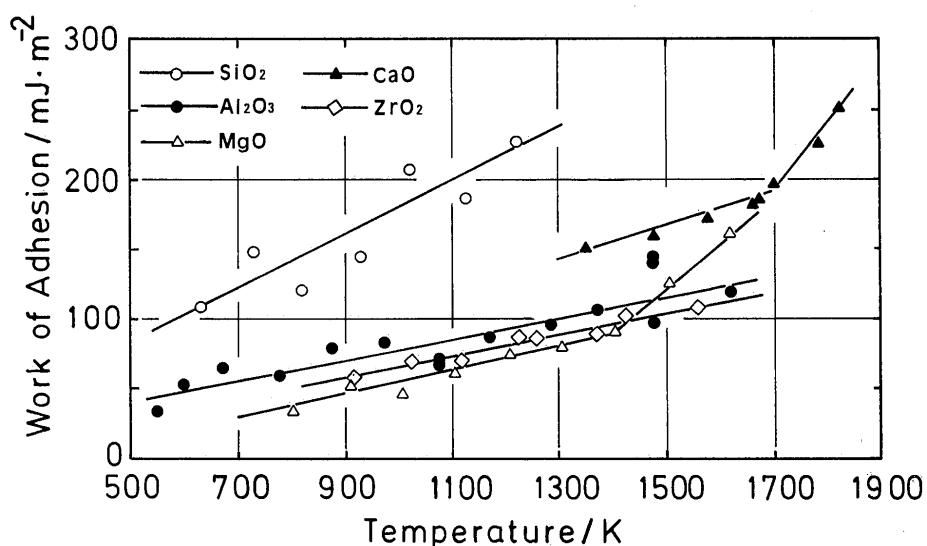


Fig.1 Temperature dependence of work of adhesion between liquid pure Sn and various oxides

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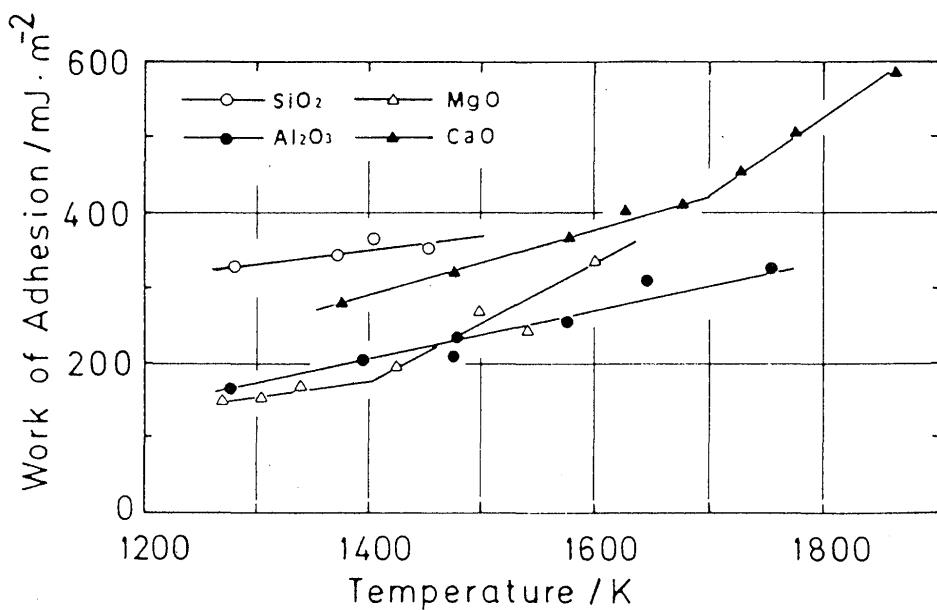


Fig.2 Temperature dependence of work of adhesion between liquid pure Ag and various oxides

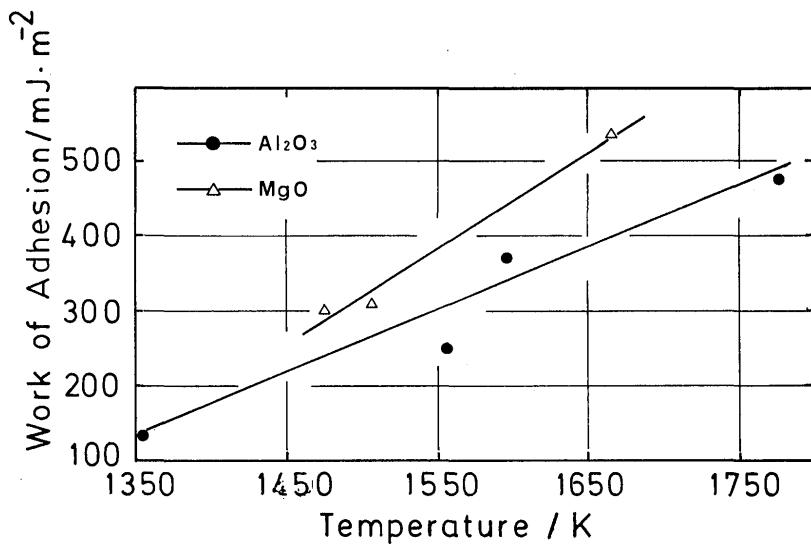


Fig.3 Temperature dependence of work of adhesion between liquid pure Au and various oxides

/ solid oxide system³⁾. It can be seen from Figs. 1 - 4 that the work of adhesions between liquid pure metals and solid oxides show a tendency to increase with the increase in temperature and also that the work of adhesion for MgO and CaO differ from that for other solid oxides, not changing a linear relationship with temperature but having refraction points in the case of MgO around 1400K, and CaO around 1700K.

The same refraction points, shown in Fig. 5, can be

seen in the Elingham diagram⁴⁾ which shows the relationship between the standard free energy change of oxide formation from element and temperature. This result can be a clear evidence for the work of adhesion having close relation to the thermodynamical stability of solid substrate.

The surface of oxides is generally thought to be covered with oxygen. When a liquid metals comes into contact with the oxide surface, it is thought that the

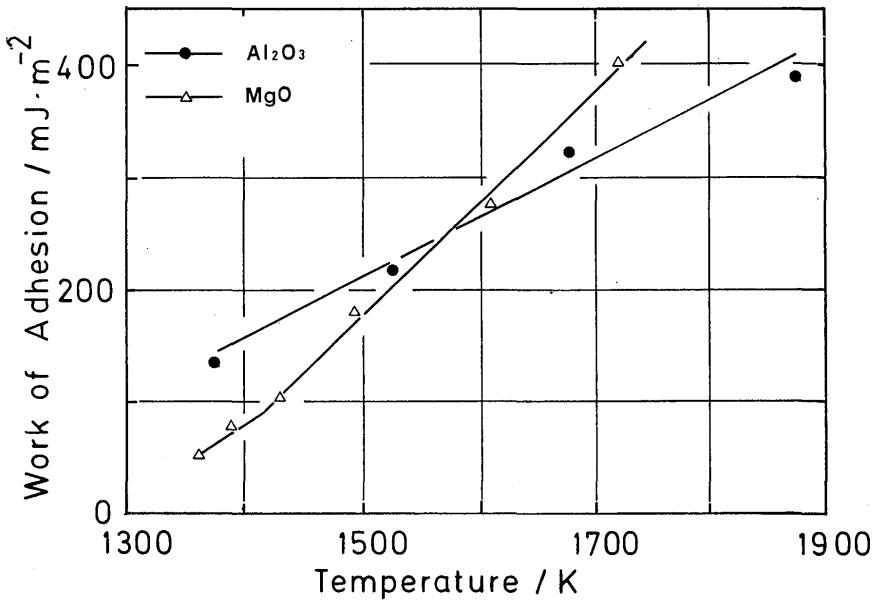


Fig.4 Temperature dependence of work of adhesion between liquid pure Cu and various oxides

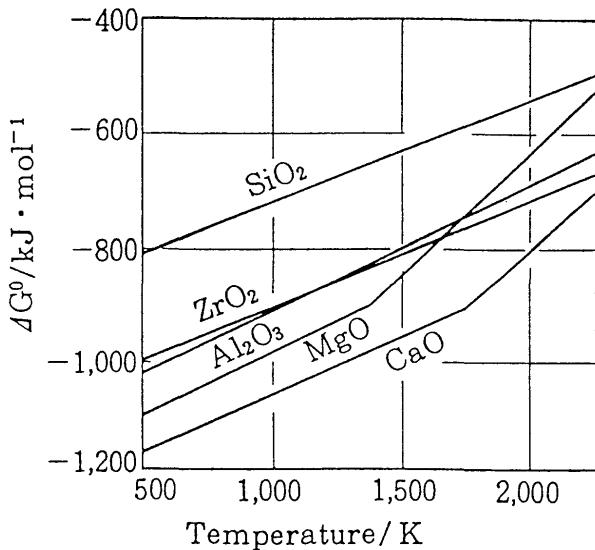


Fig.5 Standard free energy of formation of various oxides from elements as a function of temperature

affinity between the metal and the oxygen affects the wettability. The affinity between liquid metal and oxide is evaluated as a measure of the bonding strength between liquid metal and oxide, and is thought to involve a physical interaction term and a chemical interaction one.

If we define the change in surface free energy when 1 mole of liquid metal is spread to the thickness of one atom (molecule) as $W_{a \cdot mol}$, the relationship to the work of adhesion can be shown in eq. (1)⁵⁾.

$$W_{a \cdot mol} = (M / \rho)^{2/3} \cdot N^{1/3} \cdot f \cdot W_{ad} \quad (1)$$

where $W_{a \cdot mol}$ is the change in surface free energy (mJ/mol), ρ the density of solid oxide (kg/m³), M the molecular weight (kg/mol), N the Avogadro's number, f the packing coefficient, and W_{ad} the work of adhesion (mJ/m²).

When we want to calculate $W_{a \cdot mol}$ using eq.(1), the problem is how to evaluate f . This value differs of course according to the crystal structure and the crystal plane of surface. However, because all the solid oxides used were sintered ones, the crystal plane of the surface could not be decided. Therefore, here we have fixed the value of f at 1.

A relationship between surface free energy change and standard free energy change concerning to Sn and Ag is shown in Fig.6. As can be clearly seen from Fig.6, both Sn and Ag show the same tendency. Except for the CaO, the smaller the value of the standard free energy of oxide, i.e. the more stable the oxide, the smaller the change in surface free energy and thus the weaker the bonding strength between the solid oxide and liquid metal. CaO is an exception to the rule for the following reason.

Generally, oxygen ions (anions) appear at the oxide surface, and metal ions (cations) exist inside rather than at the surface. Ionic radius of anion is generally larger than that of cation, and so the anion is more easily polarized. This degree of polarization depends on the radius of the cation, and the smaller the radius, the greater the polarization. As can be seen in Table1, the ionic radii of the ions which make up the oxides used have a great deal of variation⁶⁾.

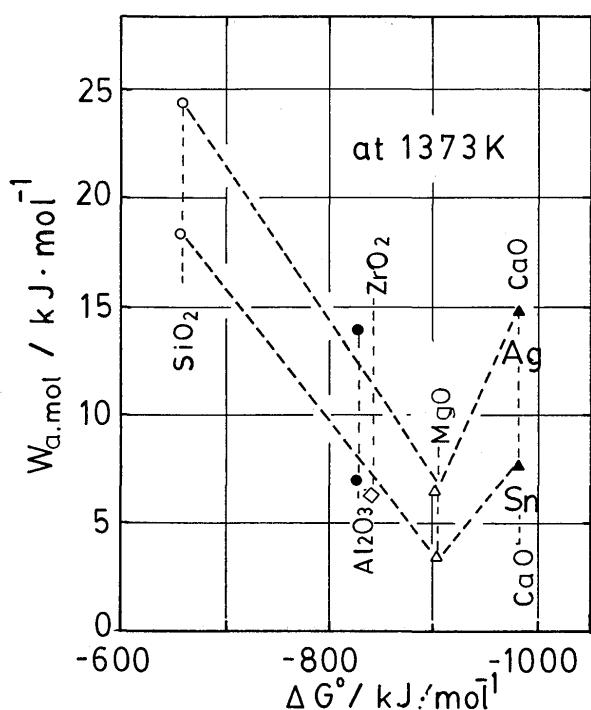


Fig. 6 Relationship between surface free energy change and standard free energy change of oxides

Table 1 Ionic radius of elements (nm)

Ion	Radius	Ion	Radius
Si	0.041	Al	0.050
Mg	0.065	Zr	0.080
Ca	0.099	O	0.140

It is clear from Table 1 that an ionic radius of Ca is the largest in the present work. Therefore, it can be expected that the degree of polarization of oxygen is the smallest at the CaO surface. This implies that ionic property is the largest at the CaO surface. When a liquid metal contacts with CaO, an electron of element of liquid metal can be strongly attracted to the oxygen ion at the surface. This caused the increasing of the work of adhesion (surface free energy change). This consideration can be applied to previous results.

Humenik et al reported that contact angles of liquid pure Ni on BeO and ThO₂ are 152° and 132° and those of liquid Fe on BeO and ThO₂ are 147° and 111°, respectively⁷⁾. It is obvious that the contact angles on ThO₂ are smaller than those on BeO in both cases.

However, it cannot be applied Naidich's¹⁾ and McDonald's²⁾ ideas to explain these results, because ThO₂ is thermodynamically more stable than BeO. It is possible to explain the results when we take into account an ionic radius difference between Be²⁺ and Th⁴⁺.

The ionic radii of Be²⁺ and Th⁴⁺ are 0.035nm and 0.102nm, respectively, and Th⁴⁺ is about 3 times larger than Be²⁺. Accordingly, it is reasonable from the viewpoint of ionic radius that the contact angles on ThO₂ is smaller than those on BeO at the oxide surface.

4.2.2 Temperature

It is sometimes difficult to describe the effect of temperature on the wettability of ceramics by liquid metals since thermodynamical stability of ceramics and metals and oxygen potential in an atmosphere on which the wettability depends are also affected by temperature.

As can be seen from Figs. 1 - 4, there is no doubt that the change of work of adhesion relates to temperature. As we have mentioned, however, that the thermodynamical stability is also a function of temperature, we cannot decide how the work of adhesion relates to temperature. We know, of course, that a chemical reaction term can be more dominant than a physical interaction term at high temperature but it is true that a degree of chemical reaction also depends on the thermodynamical stability.

It is impossible to find the effect of temperature on the wettability without neglecting that of the thermodynamical stability.

4.2.3 Atmosphere (Oxygen potential)

A lot of reports have been published concerning the effect of oxygen on the wettability of ceramics by liquid metals⁸⁻¹⁵⁾.

It has been clarified that oxygen in liquid metal and in an atmosphere significantly affects the wettability of ceramics. Two of authors measured the wettability of Al₂O₃ by liquid Ni under controlled oxygen potential and obtained an interesting result⁸⁾.

Figure 7 shows the effect of oxygen on the wettability of Al₂O₃ by liquid Ni. The contact angle of liquid Ni on Al₂O₃ increases steeply and then decreases gradually with the increasing of oxygen in liquid Ni. It can be concluded from the result that two methods exist to reduce the contact angle of liquid Ni / Al₂O₃ system. One is to decrease a oxygen content as possible as we can and the other is to increase the oxygen content to a certain amount. The different mechanism can be proposed for the decreasing contact angle. A low contact angle at the lower oxygen content can be caused by a dissociation of Al₂O₃. One might doubt that the liquid Ni reduces Al₂O₃ because Al₂O₃ is more stable than NiO. But two of

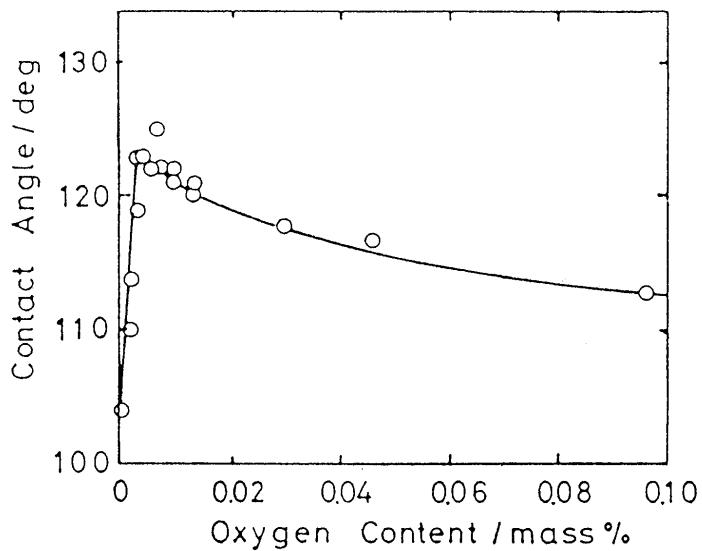
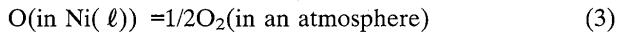
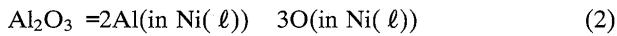


Fig.7 Effect of oxygen on the contact angle of liquid Ni on Al_2O_3 at 1873K

authors proposed the following reaction¹⁶⁾.



The dissociation of Al_2O_3 by liquid Ni cannot occur if activities of Al and O are 1. It is, however, possible to reduce the activities of Al and O in liquid Ni when we use pure Ni. Above reaction is also possible if Ni is solid and helps to obtain desirable Ni / Al_2O_3 joint¹⁶⁾. It has already been reported by many researchers that an oxidizing atmosphere is suitable for metal / oxide joining. However, joining in the oxidizing atmosphere causes an oxidation of metal and a joining strength in the oxidizing atmosphere is weaker than that in a reducing atmosphere.

Two of authors obtained that the joining strength was 84MPa in an H_2 atmosphere and 44MPa in an air atmosphere¹⁶⁾. As mentioned above, this result implies a possibility of different bonding mechanism between under the reducing atmosphere and under the oxidizing one.

Klomp reported that Ni cannot reduce Al_2O_3 and a mechanism of joining in a reducing atmosphere should be a $\text{NiO-Al}_2\text{O}_3$ bonding even in the reducing atmosphere¹⁷⁾. Kohyama et al, on the other hand, proposed that a bonding between Ni and Al_2O_3 under ultra high vacuum is a direct one between Ni and O which is a constituent of Al_2O_3 ¹⁸⁾. The ultra high vacuum is the same condition as the H_2 atmosphere in the sense of very low oxygen potential.

It can be concluded from our result¹⁶⁾ that Kohyama's proposal is more likely to be the bonding mechanism in H_2 atmosphere.

4.2.4 Surface condition of ceramics

It has been proposed the following equation for the relationship between contact angle of liquid on solid and surface roughness of solid.

$$\cos \theta' = R \cos \theta \quad (4)$$

where, θ' is an apparent contact angle, R the surface roughness factor (surface area of solid which has a rough surface / surface area of solid which has a smooth surface), θ the real contact angle.

The equation (4) is well known as Wenzel's equation¹⁹⁾ but nobody has succeeded to give a theoretical explanation. Here, we will try to introduce eq.(4).

Let us consider a free energy change and contact angle change when liquid spreads on solid which has a rough surface as in Fig.8. Here, we can write that real changes of areas of solid surface and solid-liquid interface are $-dA$ and dA , respectively. On the other hand, area change of liquid surface can be written as $dA_0 \cdot \cos(\theta + d\theta)$.

$$dF = \gamma_{LV} \cdot dA_0 \cdot \cos(\theta + d\theta) + \gamma_{SL} \cdot dA - \gamma_{SV} \cdot dA \quad (5)$$

where, dF is a free energy change in the system, γ_{LV} the surface free energy of liquid, γ_{SL} the interfacial free energy between solid and liquid, γ_{SV} the surface free energy of solid, dA_0 the apparent surface area change of solid, dA the real surface area change of solid, and θ the contact angle between solid and liquid.

The equation (5) should be zero at the equilibrium state and eq. (6) can be derived.

$$\begin{aligned} \lim (dF/dA_0) &= \lim \{ \gamma_{LV} \cdot \cos(\theta + d\theta) \\ &+ (\gamma_{SL} - \gamma_{SV})dA/dA_0 \} \\ &= \gamma_{LV} \cdot \cos \theta + (\gamma_{SL} - \gamma_{SV})dA/dA_0 \end{aligned}$$

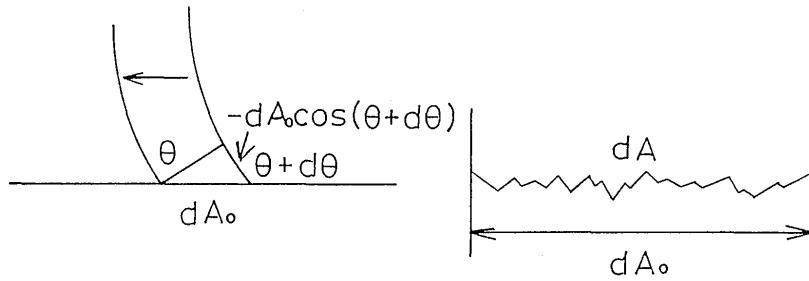


Fig. 8 Schematic diagram of the change in free energy by spreading of liquid metal

$$= 0 \quad (6)$$

We know the eq. (7) which is famous as Young's equation.

$$\gamma_{SV} = \gamma_{LV} \cos \theta + \gamma_{SL} \quad (7)$$

The equation (4) can be obtained by substituting eq.(7) into eq.(6).

The wettability is affected by not only surface roughness but also an atomic arrangement of ceramics surface²⁰⁾.

The authors measured contact angles of liquid pure Bi, Pb and Sn on MgO single crystals and found that the contact angle depends on surface orientation of MgO and the wettability is affected by an annealing of MgO.

As can be seen from Table 2, (100) plane gives the largest value of the work of adhesion and (110) plane does the smallest one. The work of adhesion between liquid metals and MgO depends on the affinity between oxygen and liquid metal at the interface and on the quantity of oxygen on MgO surface. The quantities of O²⁻ (NO₂⁻) on the (100) plane of MgO, on the (111) plane of MgO and on the (110) plane of MgO were calculated as 1.88 × 10⁻⁹ (mol·cm⁻²), 2.18 × 10⁻⁹ (mol·cm⁻²), 1.33 × 10⁻⁹ (mol·cm⁻²), respectively. It is clear that the values of the work of adhesion in Table 2 are not proportional to the quantities of O²⁻. This implies that the interaction between O²⁻ and Mg²⁺ should be taken into account, the degree of which depends on crystallographic orientation. In order to explain the crystallographic orientation dependence on the wettability, the quantity of O²⁻ on the MgO surface and the coulomb force (F) acting between O²⁻ at the surface and Mg²⁺ at the second layer of MgO were calculated.

The stronger the coulomb force, the stronger the force towards the bulk. This means that O²⁻ at the surface are unable to interact with liquid metal when the coulomb force becomes stronger. Accordingly, it is reasonable to consider a large value of NO²⁻/F yields a large value of work of adhesion. The calculated values of NO²⁻/F of the (100) plane of MgO, the (111) plane of MgO and (110) plane of MgO were 9.0 × 10⁻⁷ (mol·esu²), 6.0 × 10⁻⁷

Table 2 Work of adhesion between liquid metals and MgO single crystal (mJ/m²)

liquid metal	work of adhesion(erg/cm ²)		
	(100)	(110)	(111)
Bi	88	32	52
Pb	97	14	63
Sn	121	8	84

(mol·esu²) and 4.5 × 10⁻⁷(mol·esu²), respectively. It can be seen from Table 2 that the values of NO²⁻/F increase along with an increase in the the values of the work of adhesion. It can be assumed that the values of NO²⁻/F correspond to the ionicity of the MgO surface. Thus, it is possible to explain qualitatively the crystallographic orientation dependence of the wettability by considering the interaction between O²⁻ at the surface and Mg²⁺ at the second layer.

An annealing of ceramics also affects the wettability. It can be seen from Figs. 9-11 that heat treatment of MgO affects the wettability. Reproducibility of the contact angles of liquid Pb on annealed MgO was better than those on as-received ones. This fact suggests that the annealing which removed surface strain introduced by a polishing process produced thermodynamically more stable surface arrangements which have low surface energy.

Two of authors reported that a polishing method and an annealing of substrate affected the wettability for liquid metal/solid metal system and that electrolytic polishing and annealing prompted it²¹⁾. They concluded that strain induced by polishing was removed by electrolytic polishing or annealing, and that wettability of the substrate without strain was better than that with strain. These results correspond to those obtained in liquid Pb/MgO system.

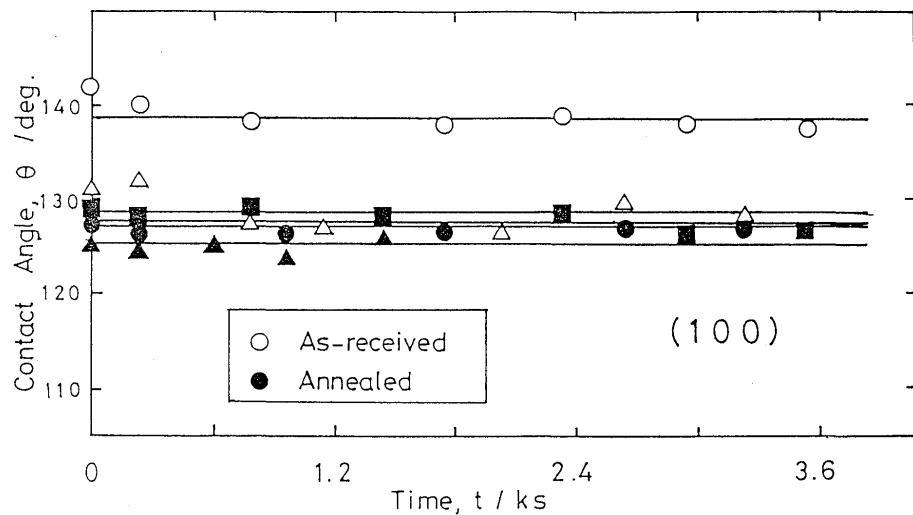


Fig. 9 Time dependence of contact angle between liquid pure Pb and (100) plane of MgO surface

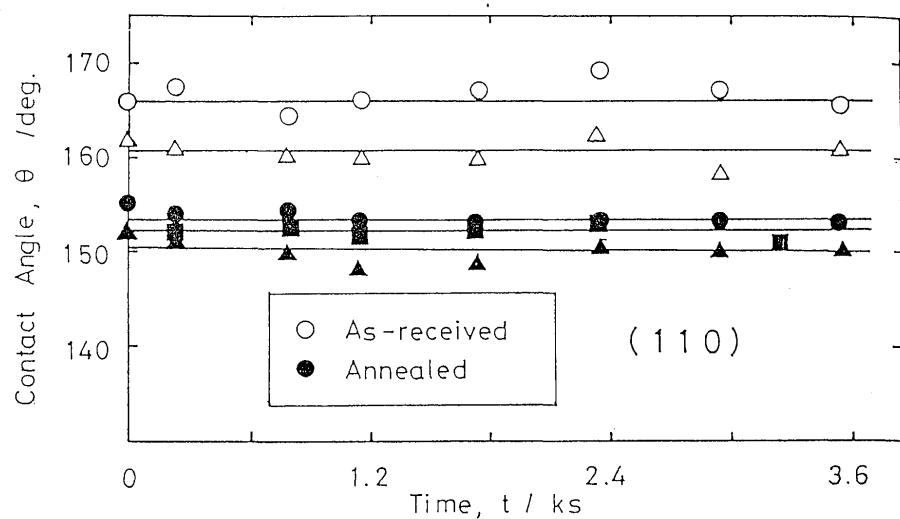


Fig.10 Time dependence of contact angle between liquid pure Pb and (110) plane of MgO surface

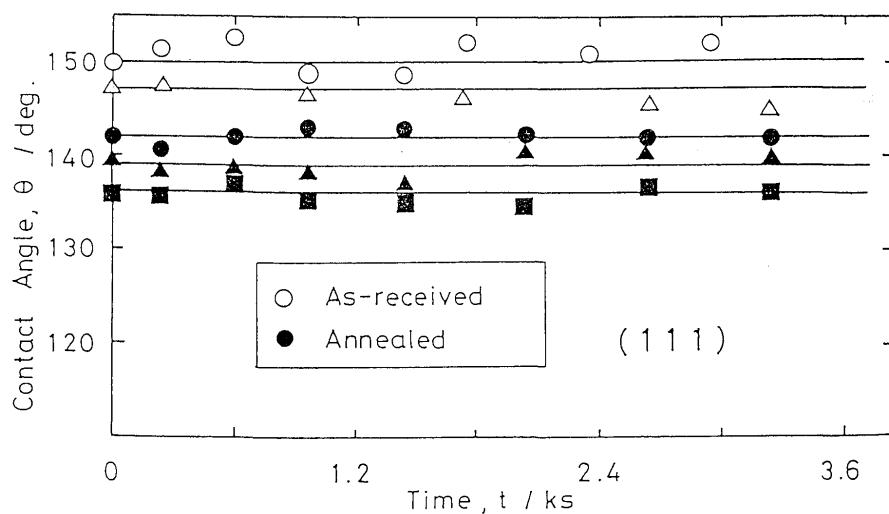


Fig.11 Time dependence of contact angle between liquid pure Pb and (111) plane of MgO surface

Accordingly, the removal of the strain on the MgO surface by annealing is considered to be one reason for a promotion of wettability.

The alteration of surface atomic arrangement of substrates by annealing may also be a reason for the promotion of wettability.

It has been reported as well that the annealing of the (110) and (111) planes of MgO for a few minutes at 1400K produced strong faceting of the (110) and (111) crystal faces²¹⁾. This report and the results of wettability measurement suggest that the structure of unstable MgO surface is transformed into a stable structure at 1400K, and these changes in the surface arrangement contribute to the wettability.

It can be concluded that there are many factors affecting the wettability of ceramics by liquid metals and sometimes it is very difficult to clarify the effect of factors on the wettability because these factors relate each other.

As we could not describe the effect of alloying elements on the wettability of ceramics by liquid metals in this review, we will describe the effect of alloying elements in the next review.

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