THE NANO-WETTING ASPECT AT THE LIQUID-METAL/SiC INTERFACE

VIDIK NANOOMAKANJA NA STIKU STALJENA KOVINA-SiC

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The wetting process on the nano-scale, as an initial and essential step in liquid metal/ceramic joining, is discussed here. Thanks to recent breakthroughs in experimental techniques with nanometre resolution, questions posed several decades ago are being looked at again. Despite recorded facts on acting mechanisms, the published results are very diverse due to the variety of materials and their structures, as well as experimental conditions, so the modeling is inevitable for process development and to overcome the multi-scale influencing parameters issues. A nano-scale wetting model have been proposed and tested on results obtained in a liquid-metal/SiC system that was published in the literature.

Keywords: wetting, modelling, nano-scale, metal/ceramic interface

Razložen je postopek omakanja na nanonivoju kot začetni in bistveni del pri spajanju staljena kovina-keramika. Zaradi sedanjih, prelomnih eksperimentalnih tehnik do nanometrske resolucije se ponovno pojavljajo vprašanja, stara več desetletij. Kljub dejstvom glede delujočih mehanizmov so objavljeni rezultati zelo različni zaradi različnosti materialov in njihovih struktur, kot tudi eksperimentalnih razmer. Zato je neizogibno modeliranje razvoja procesov, da se preseže številne večdimenzijske vplivne parametre. Na podlagi literaturnih podatkov iz sistema staljena kovina-SiC je bil predložen in preizkušen model omakanja na nanonivoju.

Ključne besede: omakanje, modeliranje, nanopodročje, stik kovina-keramika

1 INTRODUCTION

Although such different materials in terms of heat and electrical conductivity, as well as hardness, ductility, wear or corrosion resistance, metals and ceramics have integrated the advantages of their differences in many modern applications when operating together. Wetting as the initial and inevitable phenomenon of the liquid metal to ceramic joining process have been investigated, both experimentally and theoretically for more than three decades.[1–5] In the most recent decade, experimental techniques enabled an insight into wetting phenomena at high resolution, i.e., at the nanoscale.[6] Nevertheless, modeling is still a required method for wetting-process prediction. Despite, or simply because of modern experimental techniques, any investigation of metal/ceramic wetting mechanisms acting on the micro and nano levels is still demanding, both experimentally and theoretically.[5,7,8] These mechanisms are important for understanding metal/ceramics interfacial bonding and further process development.[3] The trend in several fields of science today is miniaturization and developing towards the nano-scale, both for the sake of sensitive processes and for lowering the costs; whereas for metal/ceramic systems the intention is the miniaturization of electronic devices.[8,9] This pushed SiC to the center of investigations again. Besides superconductivity, it has a very low coefficient of thermal expansion and an absence of phase transformations at operating temperatures, enabling the observed crystal structure to be stable. Together with new technical developments, new theoretical concepts are also required.

There are several theories used to describe interface bonding in the two adjacent components, i.e., liquid metal and solid ceramic, materials that are diverse due to the different types of atomic bonding.[5] One of the first theories was confined to reactive wetting, known as the 'reaction product control' theory, claimed that the interface reactions take control over the wetting mechanism at the interface,[1,10] while the opposite theory claimed that chemical reactions are not crucial for controlling the wetting phenomenon, but the capillary effects and adsorption of metals onto the ceramic substrate, with triple line ridging[11,12]. During years of research, theories were supported by experimental data, some statements were reconsidered,[13,14] and plenty of influential parameters were investigated. For the sake of plenty of investigated metal/ceramic systems and different approaches, there were variations in the experimental work, as well as in the suggested theoretical models. For the comprehensive modeling, both the physical and chemical approaches should be taken into account, as well as the mechanisms acting at the nano scale.

2 A NANO-SCALE MECHANISM – THE FRACTIONAL SURFACE APPROCAH

The macroscopically measured contact angle, θ, defined by Young's equation (1), is usually interpreted as the bonding quality of the metal/ceramic interface, but this criteria is valid only up to the micron scale. The atomic structure of the liquid metal and of the substrate becomes important on the nano-scale, and nano-wetting properties have an important influence on the macroscopic wetting behavior of liquids on solid surfaces.[4,6,8]

The wetting properties of the liquid metal/ceramic interface are strongly affected by the composition of the solid and liquid components, the roughness and other irregularities on the macro level, or grain-boundary grooves and lattice pits at the micro-scale, the surface pattern of the ceramic substrate, and either the reactive or non-reactive wetting, by the mechanisms occurring at the nano scale, including thermal influences.[4–7,15–17]

Although the geometrically structured substrates were a matter of interest for years[18] at macro and micro scale, they can be investigated in a new light, since the recent development of experimental techniques at the nano level, as well as of accompanied theories.[4,6,19]

It is shown that a change in the type of liquid metal/substrate interface, in the same system (Ni-Si/C system with a formed reaction layer of SiC and hence an interface change), leads to a remarkable change in the wetting: from contact angles much higher than 90 ° to contact angles in the range 20–40 °.[20] This refers to the macroscopically measured contact angle θ.

There is a wide range of reported measured contact angles for the pure liquid metals in a contact with SiC, for different temperatures, in a literature review.[3] A dramatic change in the contact-angle values for the majority of reactive metals is normally used in metal/ceramic brazing is registered, even reflecting in a wetting-nonwetting transition for the same metal with the temperature change. The situation is more complicated when the liquid metal is in fact an alloy.

Recent *in-situ* experiments at the nano level brought into connection the high traveling angle of the molten metal over the SiC basal plane with a high interfacial energy between the molten metal (Ti) and the SiC.[6] So, the nano-level analysis can also start from the interfacial energies relation in the Young's equation (1):

$$\cos \theta = \frac{\gamma_{SA} - \gamma_{LS}}{\gamma_{LA}} \qquad (1)$$

where γ_{SA}, γ_{LS} and γ_{LA} are solid-air (i.e., the corresponding atmosphere), liquid-solid and liquid-air interfacial energies, respectively. Combining this with the Cassie and Baxter relationship for rough surfaces,[18] modified with two coefficients concerning the surface area, one can see that the net energy in the system is expressed according to Equation (2):

$$E_N = f_2 \gamma_{LA} - f_1 \gamma_{LA} \cos \theta = \gamma_{LA}(f_2 - f_1 \cos \theta) \qquad (2)$$
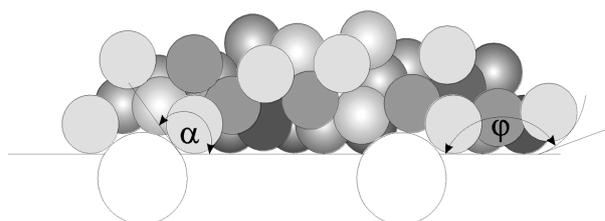
Figure 1: The liquid-metal atoms in contact with the ceramic-substrate atoms
Slika 1: Atomi staljene kovine v stiku z atomi keramike v podlagi

where f_1 is the total area of the solid-liquid interface and f_2 is the total area of the liquid-air interface (fractional surface factors).

Using the energy Equation (2), the cosine of the apparent contact angle, θ_A, for the geometrically structured surface, can be expressed as:

$$\cos \theta_A = -\frac{E_N}{\gamma_{LA}} = f_1 \cos \alpha - f_2 \qquad (3)$$

The atomistic arrangement of atoms in a liquid metal is not entirely random. During melting the crystal structures are being broken down, and the average packing density becomes smaller than in the solid state. The interatomic forces keep trying to establish the original arrangement, at the same time being disturbed by the thermal motion of the atoms. So, the melt is much more like the crystal than the completely random state of a gas. **Figure 1** shows the liquid metal atoms in contact with the ceramic substrate atoms, with the apparent contact angle φ and advancing contact angle between the liquid metal atoms and the ceramic substrate (α). Several authors[21] found that in the liquid Cu/SiC system, the liquid Cu spreads over the hexagonal crystal structure of β-SiC, maintaining a hexagonal shape. Since SiC has over 250 crystalline forms, it is necessary to develop a model taking into account the crystal lattice and the planes' orientation.
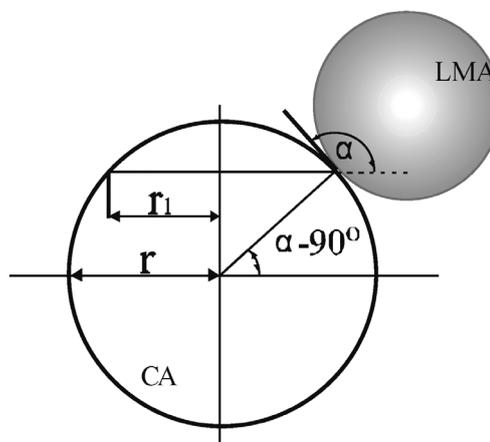
Figure 2: Angles describing the position of liquid metal atoms (LMA) in contact with the ceramic substrate atoms (CA)
Slika 2: Koti, ki opisujejo položaj atomov v staljeni kovini (LMA) v stiku z atomi iz keramike v podlagi (CA)

At the atomistic level, the new dimensions of f_1 and f_2 can be introduced. Areas f_1 and f_2 can be derived from the value of the angle α, the contact angle between the atoms of the metal and the ceramic, as denoted in **Figure 2**, and the atom packing density s in the plane of the crystal lattice along which the contact with the liquid metal is established.

If the reciprocal atom packing density is denoted with s, and expressed through the atomic radius in the plane along which the wetting process occurs in a monocrystal, then the total plane area (P) will be:

$$P = s \cdot \pi \ r^2 \tag{4}$$

P_1 is the ceramic atom surface area in contact with the metal atoms:

$$P_1 = 2\pi r^2 \cdot \left[1 - \sin(\alpha - 90°)\right] \tag{5}$$

while P_2 is the area of the liquid metal at the metal/ceramic interface, which is not in contact with the crystal lattice atoms:

$$P_2 = P - \pi r_1^2 \tag{6}$$

The contact point of the liquid metal atoms in contact with the solid substrate atoms is at the distance r_1, shown in **Figure 2**. According to **Figure 2**, it can be written:

$$r_1 = r \cdot \cos(\alpha - 90°) \tag{7}$$

and hence the f_1 and f_2 are:

$$f_1 = \frac{P_1}{P} = \frac{2 \cdot \left[1 - \sin(\alpha - 90°)\right]}{s} \tag{8}$$

$$f_2 = \frac{P_2}{P} = \frac{s - \cos^2(\alpha - 90°)}{s} = 1 - \frac{1}{s} \cos^2(\alpha - 90°) \tag{9}$$

Similar to our calculations, there is an expression for the apparent contact-angle cosine on a super-hydrophobic surface, Equation (10).[22] With the same Cassie-Baxter approach, it is postulated that the measured contact angle is a sum calculated for n surfaces:

$$\cos \theta_A = \frac{1}{\gamma_{LA}} \sum_{n=1}^{N} f_n (\gamma_{n,SA} - \gamma_{n,LS})$$
$$\text{where } \sum_{n=1}^{N} f_n = 1 \tag{10}$$

where γ_{SA}, γ_{LS} and γ_{LA} are the interfacial energies, as described previously, and f_n is the fractional coverage of the nth chemical species.

There is a coincidence in the wetting approaches at the nano level, although contradictory processes have been observed: the wetting and super-non-wetting. It has been observed that both wetting processes can be enhanced, i.e., modified by introducing the geometrically structured surface approach.

3 RESULTS AND DISCUSSION

Knowing the f_1 and f_2 factors in their new, nano-scale meaning, the apparent contact angle on a nano-structured
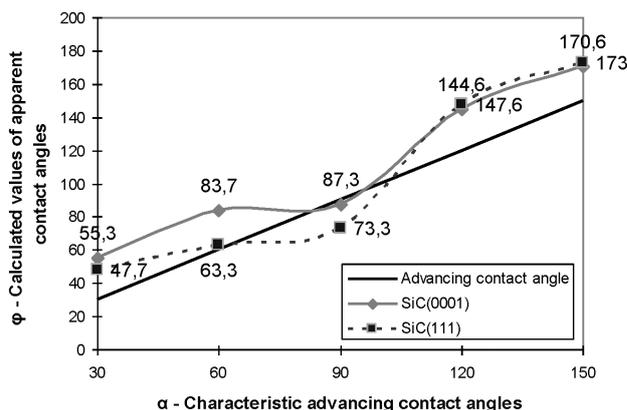
Figure 3: Comparison between calculated values of apparent contact angles φ and the characteristic advancing contact angles α for different orientations of the substrate planes
Slika 3: Primerjave med izračunanimi vrednostmi navideznih kotov stika φ in značilnih napredujočih kotov kontakta α pri različnih orientacijah ravnin podlage

surface can be calculated according to Equation (3), for contact angles larger than 90 ° (the non-wetting case). For the wetting case, angles smaller than 90 °, this equation is modified by using supplementary angles to the apparent contact angles, due to the different substrate (CA) and the position of the liquid metal atoms (LMAs), and hence the different geometry. So, Equation (3), according to **Figures 2** and **3**, becomes (11):

$$\cos \varphi = f_1 \cos(180° - \alpha) - f_2 \tag{11}$$

Most researchers deal with the α-SiC(0001) and β-SiC(111) crystallographic planes, so this calculation is based on the determined atomic packing factors for these types of crystal lattice, although there are more than 250 different polytypes of SiC.[23,24] The obtained results are summarized in **Figure 3**.

The influence of the substrate planes' orientation on the calculated values of the apparent contact angles is clear in **Figure 3**. A deviation from the straight line, representing the characteristic advancing contact angles, differs more between the two different SiC planes for the wetting case, i.e., for angles smaller than 90 °, in comparison to the non-wetting case, where the lines are almost overlapped. It is clear that the minimum discrepancy between the advancing and the apparent calculated contact angle is around 90 °, i.e., where the transition wetting–non-wetting occurs. Besides, the trend is somewhat similar, but shifted, for both the α-SiC(0001) and β-SiC(111) crystallographic planes. This is due to the similarity in the configuration between those two crystallographic planes, already reported by others.[3]

It must be emphasized that this consideration is restricted to the non-reactive wetting case. During the formation of the new reaction product at interface, the distortion of the substrate lattice at the interface is inevitable, so other specific lattice factor calculations would have to be performed.

4 CONCLUSIONS

The wetting effect on the nano-scale depends on the structure of the crystal lattice and the planes' orientation according to the proposed model tested with measured apparent contact angles.

This is an aspect of possible liquid-metal/ceramic interface phenomena and this approach should contribute to a better understanding of the complex interface wetting behavior and should help in predicting the wetting modification on the nano-scale. But there is still the need for further investigations and modeling of the wetting at the liquid metal/ceramic interface, since quite different mechanisms take place at the nano level, compared to the well-established theories based on macroscopic contact-angle measurements.

Acknowledgement

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