Fundamental Study on Wettability of Pure Metal by Liquid Sodium

Jun-ichi Saito, Hideo Shibutani and Yohei Kobayashi

Abstract Liquid sodium is used as a coolant of a fast reactor owing to its high thermal conductivity and high melting temperature. Wettability is an important property for designing the apparatus of the fast reactor. It is well known that the wettability of liquid sodium changes owing to factors such as surface roughness and type of metal. This study proposes an atomic interaction between metal and liquid sodium related to wettability. The purpose of this study is to understand the wettability of pure metal by liquid sodium by using both experimental and theoretical approaches. High-purity metal plates of titanium, vanadium, iron, nickel copper, and molybdenum were used in the experiment. Wettability was evaluated using the contact angle obtained using the tangent method, and simple surface models were constructed for theoretical calculation. The contact angle was evaluated using two kinds of atomic bonds, and the result showed a relation between the contact angle and the atomic bond.

Keywords Liquid sodium · Wettability · Contact angle · Atomic bonding · Electronic structure

Purpose

Liquid sodium is used as a coolant of a fast reactor because of its high thermal conductivity and high melting temperature. Liquid sodium is always in contact with a lot of equipment and pipes in a plant, and there is a difference in the performance of the contact state required by equipment. For example, it is required that the heat exchanger tubes in the heat exchanger and sodium oxide trap mesh in the cold trap

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J. Li et al. (eds.), *Characterization of Minerals, Metals, and Materials 2020*,
The Minerals, Metals & Materials Series,
https://doi.org/10.1007/978-3-030-36628-5_55

have good wettability. On the other hand, it is required that sodium pipes and a part of valves have low wettability. If the wettability of the surface can be controlled, equipment performance improves. The wettability of structure materials by liquid sodium is an important property in designing the apparatus of the fast reactor. It is well known that wettability is affected by factors such as surface roughness and type of metal [1–3]. The purpose of this study is to understand the wettability of pure metal by liquid sodium by using both experimental and theoretical approaches.

Experimental Evaluation of Wettability

Experimental Procedure

High-purity metal plates of titanium, vanadium, iron, nickel copper, and molybdenum were used in an experiment to evaluate wettability. Stainless steel (SUS304), which is the typical structural material for the fast reactor, was utilized as the reference material. High-purity sodium was also used in the experiment to avoid an adverse impact of impurity elements to surface tension. The experiment was carried out in a grove box filled with high-purity argon gas because the chemical reactivity of liquid sodium with oxygen and moisture is very high. The oxygen and moisture concentrations in argon gas were less than 3 and 0.54 ppm, respectively. Wettability was evaluated using the contact angle obtained using the tangent method. The temperature of the metal plate and liquid sodium during the experiment was 140 °C. Experiments were repeated more than three times, and the contact angle was evaluated using the average of these experimental values.

The surface roughness values of all of the plates used in the experiment were evaluated using Mitutoyo SJ-410. A typical result of nickel plate surface roughness measurement is shown in Fig. 1. The arithmetic mean roughness (Ra) was

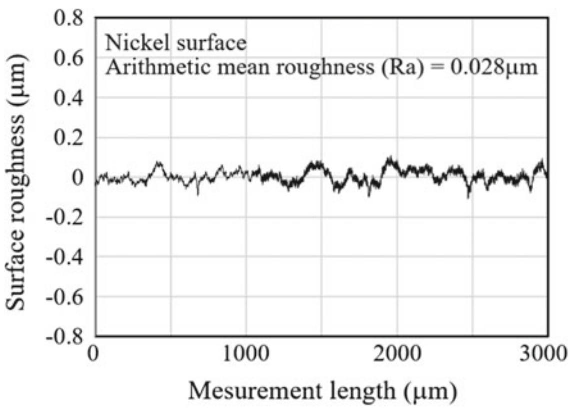


Fig. 1 Surface roughness of the nickel plate used in the experiment

0.028E−6 m. All of the plates used in the experiments had similar surface roughness values to that of nickel. Hence, it could be suggested that surface roughness has a negligible effect on wettability in this study.

Experimental Result

The experimental result of a sodium droplet on a titanium plate is shown in Fig. 2. It was confirmed that there was no oxidation of the droplet because of its mirror surface. Contact angles were measured using both A and B sides of this picture. The average value of A and B was defined as the experimental value.

The experimental results of contact angles for each metal plate with liquid sodium are shown in Fig. 3. There is a small variation of experimental values for each metal,

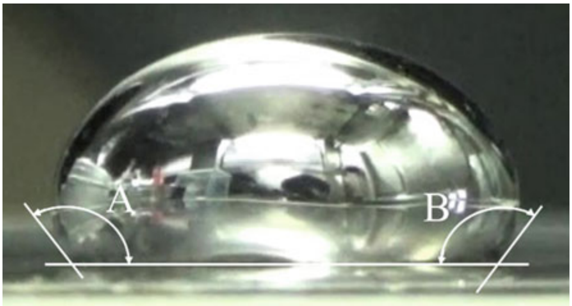


Fig. 2 Sodium droplet on the titanium plate

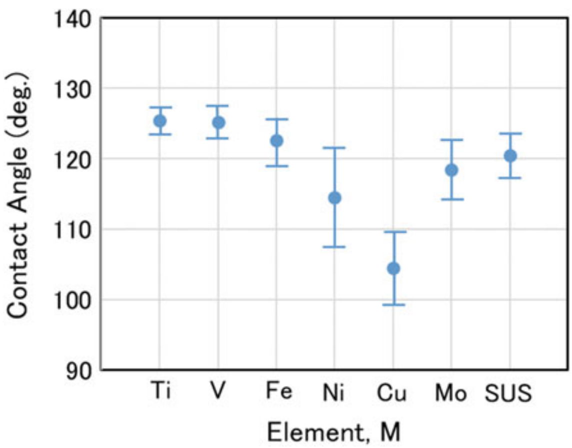


Fig. 3 Change of contact angle by plate metal

but its change depends on the melting temperature of each metal. It is interesting that the trend of change depends on the periodic table. The change of the contact angle decreases as the atomic number increases. This possibly means that the contact angle relates to the atomic interaction between metal of the plate and sodium.

Calculation of the Electronic Structure of the Interface

Molecular Orbital Calculation

An electronic structure of the interface between metal and sodium was calculated to understand atomic interactions. The discrete variational (DV)–$X\alpha$ molecular orbital method [4–7] was used in the calculation of the electronic structures of the interface.

Calculation Model of the Interface

Simple surface models of the interface were constructed for the calculation. A schematic representation of the wetting state of the metal plate with liquid sodium is shown in Fig. 4 using a simple atomic model. There are three kinds of atomic bonds in this interface. One is the M–M bond between metal and metal in the metal plate, which corresponds to the surface tension of metal. Another bond is the M–Na bond between metal and liquid sodium, which corresponds to the interface tension

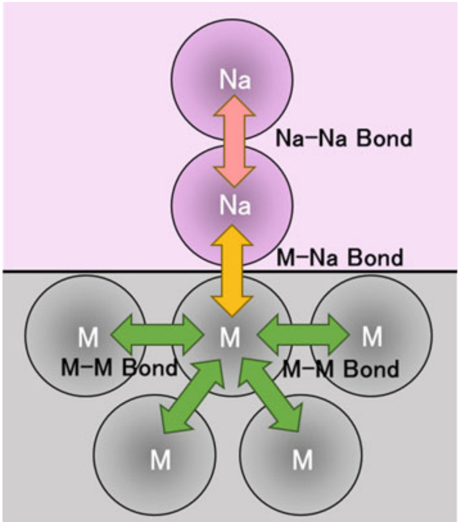


Fig. 4 Schematic of the atomic level of the wetting surface

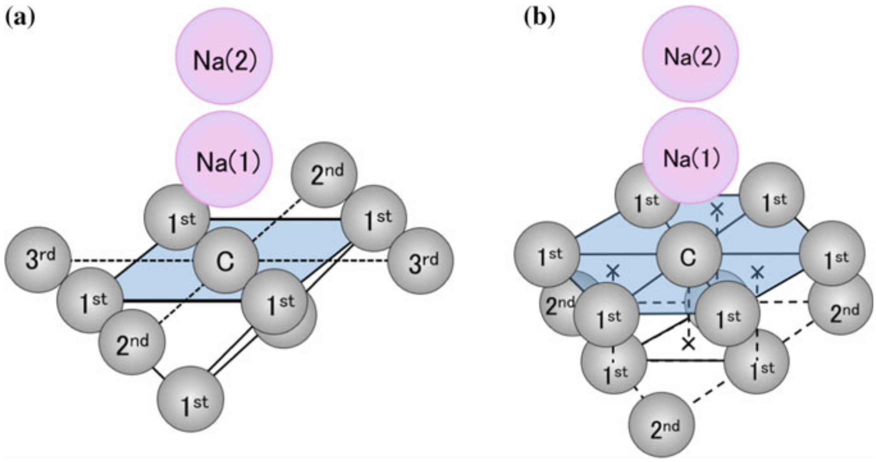


Fig. 5 Cluster models used for electronic structure calculation: **a** body-centered cubic type and **b** face-centered cubic or close-packed hexagonal crystal type

between solid and liquid. There is also the Na–Na bond between liquid sodium and liquid sodium, which corresponds to the surface tension of liquid metal. If the surface condition is the same as the surface roughness and oxidation layer, it is expected that wettability depends on atomic interaction. On the basis of this atomic model of the interface, a cluster model for calculation was constructed.

The cluster models used in the calculation are shown in Fig. 5a, b. Two types of the interface model were constructed because there are three types of crystal structure (body-centered cubic, face-centered cubic, and close-packed hexagonal crystal) of the metal plate. The same cluster model is used for the face-centered cubic or close-packed hexagonal crystal because the difference is only in layer stacking. Figure 5a shows the cluster model for a body-centered cubic metal. Figure 5b shows the cluster model for metal possessing a face-centered cubic or close-packed hexagonal crystal. Sodium atom is located on the centered plate metal atom. This location is called on-top site and represents the general contact site between two kinds of metal.

Calculation Results

Electron Density of States

The electron density of states of the iron and sodium interface is shown in Fig. 6. From these figures, most of the electronic density of states near the Fermi energy level is composed of the Fe–3d band, Na–3s band, and Na–3p band. In particular, the Fe–3d band is located near the Fermi energy level (Ef). The main features shown

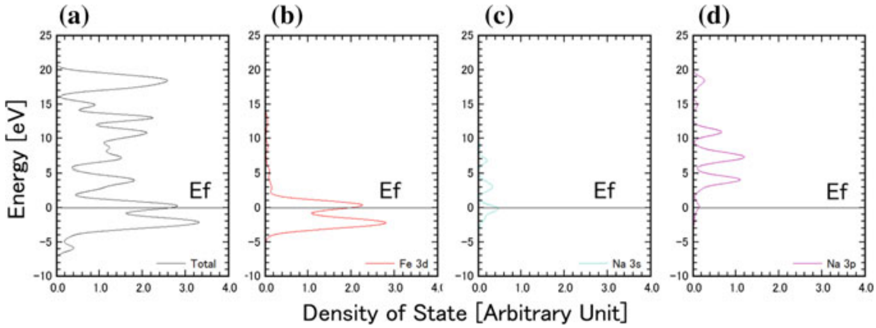


Fig. 6 Electron density of states of the interface between the iron plate and sodium

in Fig. 6b for the Fe–3d band quite resemble the results obtained from the band calculation [8–10] despite the use of the small cluster model shown in Fig. 5a.

Charge Transfer

The calculation results for ionicity are shown in Table 1. Ionicity expresses the charge transfer between atoms. A negative value means receiving electrons, and a positive value means releasing electrons. The centered metal atom and the first neighbor atoms have negative iconicity, whereas the second neighbor atoms and sodium atoms almost have positive ionicity. It is clear from this result that the charge transfer took place from the surrounding second neighbor metal atom and sodium atom to the center and the first neighbor atoms. The amount of charge transfer relates to the difference in the electronegativity of metal and sodium.

Table 1 Ionicity of each atom in the cluster model

Plate metal	Atom				
	Center	1st neighbor	2nd neighbor	Na (1)	Na (2)
Ti	−0.1774	−0.0633	0.1488	−0.1310	0.0717
V	−0.2276	0.0087	0.1919	−0.0649	0.0501
Cr	−0.1449	−0.0412	0.2008	−0.0642	0.1055
Fe	−0.1395	−0.0337	0.1018	0.0224	0.1613
Ni	−0.1689	−0.0838	0.0541	0.1267	0.1775
Cu	−0.1418	−0.0472	0.0169	0.1590	0.1693
Mo	−0.2606	−0.0144	0.0432	0.0497	0.2110

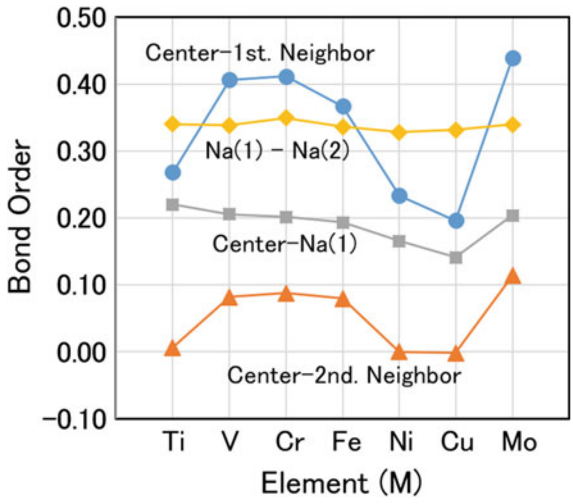


Fig. 7 Change of bond order with plate metal

Atomic Bonding

The atomic bonding of the interface is shown in Fig. 7. The vertical axis, which is the bond order, denotes the strength of atomic bonding. When the bond order is large, the atomic bonding force between atoms is strong. This figure shows that the bond order between the center atom of the plate metal and the first neighbor atom is larger than the other bond orders, and it changes with the atomic number. The bond order between the center atom and the second neighbor atom is very small. These results mean that the atomic bonding of the surface metal largely depends on the kind of metal. It is interesting that the bond order between the center atom and the sodium atom on the center atom changes with the atomic number of metals. It means that the atomic bond strength of the interface is influenced by the kind of metal and that wettability is influenced by the atomic bonding of the interface. The bond order between sodium atoms is almost constant, and this result means that the atomic bonding between sodium atoms is not influenced by the kind of metal. This calculation result shows that the atomic bond of the interface plays an important role in understanding interface behavior (Fig. 7).

Relationship Between Wettability and Atomic Interaction of the Interface

This study considers the relation between the contact angle and atomic interaction. The contact angle shown in Fig. 8 is expressed by Young's equation [Eq. (1)] [11].

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta. \tag{1}$$

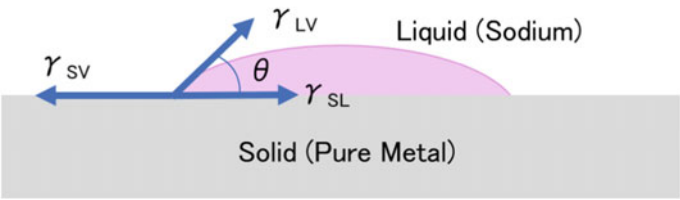


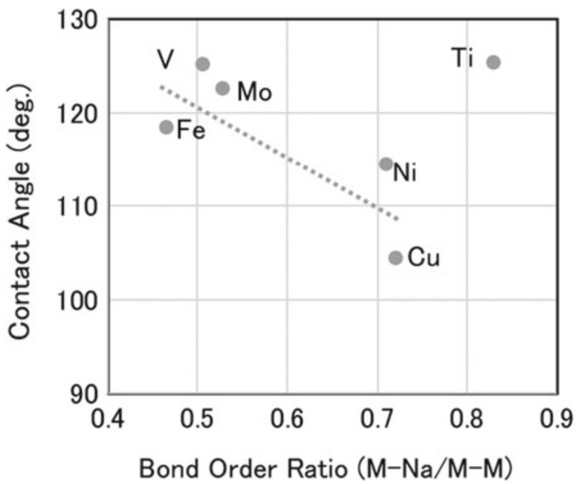
Fig. 8 Schematic of the contact angle and surface force

In this equation, the surface tension of plate metal γ_{SV} corresponds to the atomic bonding between metal atoms of the present calculation. The surface tension of liquid sodium γ_{LV} corresponds to the atomic bonding between sodium atoms, and the interface tension between plate metal and liquid sodium γ_{SL} corresponds to the atomic bonding between the plate metal atom and sodium atom.

The contact angle was evaluated using the calculated atomic bonding. The atomic bonding between sodium atoms remains almost the same with the kind of plate metal in Fig. 6. Therefore, it hardly affects wettability. On the other hand, the atomic bonding of the interface between the plate metal atom and sodium atom and the atomic bonding of the surface between plate metal atoms are very important in theoretically understanding wettability because they change with the kind of plate metal. The contact angle was evaluated using the atomic bonding between plate metal atoms and the atomic bonding between the plate metal atom and sodium atom. The evaluated results are shown in Fig. 9.

In this figure, the vertical axis denotes the contact angle, and the horizontal axis denotes the bond order ratio. It is clear that the contact angle decreased with the increase of the atomic bonding ratio. When the atomic bonding between plate metal and sodium is stronger than that between metals, the contact angle becomes smaller.

Fig. 9 Relationship between contact angle and bond order ratio



In other words, compared to the surface tension of the plate metal, when the interface tension between the plate metal and sodium becomes stronger, wettability becomes good. From these results, it is expected that the atomic bonding of the interface affects wettability. However, the contact angle of the titanium plate is not consistent with this concept. It is considered that the following reasons cause this inconsistency. In general, the surface of metal has a very thin oxidation film. Sodium has high reducing character, so when liquid sodium comes into contact with metal, the oxidation film on the metal disappears. By the reduction of the oxide film, liquid sodium comes into direct contact with metal. However, titanium oxide is thermodynamically more stable than sodium oxide. Titanium oxide remains on the metal, and the titanium plate does not come into direct contact with liquid sodium. The experimental results of the titanium plate are not a true value and include the value of the oxide film. For this reason, it is expected that the experimental result for titanium is not consistent with the calculated atomic bonding.

Conclusion

The experiments of wettability and the calculation of the electronic structure were carried out in order to understand the wettability of pure metal by liquid sodium. The contact angles for wettability were evaluated using atomic bonding. As a result, it became clear that there was a relation between the contact angle and atomic bonding.

Acknowledgements We greatly appreciate the contribution of Hana Ishiguro, a student at the National Institute of Technology, Maizuru College, who helped to measure the surface roughness of specimens.

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