WETTING OF SOLIDS WITH DIFFERENT TYPES OF CHEMICAL BONDS BY A EUTECTIC NICKEL–SULFUR MELT

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Nickel alloys are usually considered to be the best catalysts for synthesizing diamond from graphite. Eutectic Ni–S alloys are interesting in connection with their low melting point (635°C). The quantity that determines the number and rate of growth of nucleating crystallization centers is the interfacial energy at the solid-liquid boundary \( \sigma_{sl} \), which can be calculated from the results of wetting experiments. It is interesting to examine wetting, adhesion, and contact interaction at the phase boundary between an Ni–S melt and graphite and diamond. To explore certain scientific and practical aspects of the theory of surface and contact phenomena, it is useful to conduct similar studies of other solids characterized by different types of chemical bonds (mono- and polycrystalline \( \text{Al}_2\text{O}_3 \), \( \text{ZnSe} \)).

Detailed studies of contacts with solids have been performed only for pure metals and binary and ternary alloys of the inactive metal (base) — active metal (additive) type. There has not been enough research into alloys based on active metals. Our goal here is to study surface and interfacial phenomena at the phase boundary in a solid of a different physicochemical nature — a low-temperature eutectic Ni-S melt. We studied the following systems: graphite — Ni–S melt; mono- and polycrystalline \( \text{Al}_2\text{O}_3 \) — Ni–S melt; monocrystalline \( \text{ZnSe} \) — Ni–S melt; diamond — Ni–S melt. As is known, graphite and diamond are characterized by a covalent bond in solid form, while \( \text{Al}_2\text{O}_3 \) and \( \text{ZnSe} \) have ionic bonds as solids.

Wetting was studied by the stationary drop method on a standard vacuum unit \([1]\). Studies were conducted in argon at 700-800°C. An alloy of eutectic composition (67.5% (mass) \( \text{Ni} \) — 32.5% (mass) \( \text{S} \)) was obtained in an arc furnace with a nonconsumable tungsten electrode in a protective argon medium at a pressure of \( 10^5 \) Pa. As the substrates, we used polycrystalline graphite MPG-6, natural diamonds from the Yakutsk deposit (face III), leucosapphire, polycrystals of \( \text{Al}_2\text{O}_3 \), and single crystals of \( \text{ZnSe} \).

We used the experimental dependences of contact angle \( \theta \) on temperature to calculate the adhesion work \( W_a \) and interfacial energy \( \sigma_{sl} \) of the system (Fig. 1). Here, we used data on the surface tension of sulfide-nickel alloys obtained in \([2]\).

In the investigated system, sulfur is highly surface-active and lowers interfacial energy from the value of 1780 mJ/m\(^2\) (\( T = 1500^\circ\text{C} \)) for pure nickel to 540 mJ/m\(^2\) (\( T = 800^\circ\text{C} \)) for the eutectic Ni–S melt. The effect of temperature on this quantity is negligible. Values of interfacial energy equal to 2500 and 3355 mJ/m\(^2\) were calculated in \([3]\) for graphite and diamond. We took the value 905 mJ/m\(^2\) for \( \text{Al}_2\text{O}_3 \). Monocrystalline \( \text{ZnSe} \) was studied only at 850°C, in connection with its instability at higher temperatures. The contact angle was 105°C, while adhesion work was 400 mJ/m\(^2\).

It was established that the contact angles of graphite, diamond, and an \( \text{Al}_2\text{O}_3 \) polycrystal are quite large and decrease negligibly with an increase in temperature. Adhesion work increases slightly with temperature. Thus, the interaction at the interface is determined mainly by Van der Waals forces. As is known, pure nickel wets graphite (a material with a bond of the metallic-covalent type) with a contact angle of 45°. The addition of 32.5% (at.) sulfur to nickel increases the contact angle to 125°. Here, adhesion work decreases from 3000 to 220 mJ/m\(^2\). To explain these results, it will probably be necessary to use data on the thermodynamic activity \( a \) of nickel in the given melt. This quantity characterizes the rate of reaction of the components of the melt. According to \([4, 5]\), at the indicated melt concentration, the negative effect of activity deviates significantly from the effect estimated on the basis of Raoult's law \( (a_{\text{Ni}} = 0.14) \). This is evidence of the strong bond sulfur (A) forms with the metal (B), i.e. the reaction is stronger for components AB than for AA and BB. Thus, despite the
Fig. 1. Temperature dependences of the contact angle (a), adhesion work (b), and interfacial energy (c) of solid – Ni–S melt systems. 1) Graphite; 2) diamond; 3) single crystal of Al₂O₃; 4) polycrystal of Al₂O₃.

relatively high affinity of pure nickel to carbon, it does not manifest any interfacial activity in the alloy. In the system with Al₂O₃ (a material with ionic chemical bonds), the addition of 32.5% (at.) S to nickel increases \( \theta \) from the value of 112° for pure nickel to 135° for the eutectic alloy; here, adhesion work decreases from 1100 to 170 mJ/m². It must be assumed that the latter is also related to the significant reduction in the thermodynamic activity of nickel in the melt.

The lowest contact angle was seen for monocrystalline ZnSe, probably due to the reaction ZnSe + S = ZnS + Se at the phase boundary. This can be attributed to the fact that the free energy of formation of ZnSe (\( \Delta G = 174 \text{ kJ/mole} \)) and ZnS (\( \Delta G = 180 \text{ kJ/mole} \)) [6] is low, i.e. the probability of occurrence of this reaction is fairly high. Thus, only in the given system is adhesion work due to chemical processes occurring at the interface, in addition to Van der Waals forces.

The high calculated values of interfacial energy \( \sigma_{sl} \) at the graphite (diamond) — Ni–S melt boundary make it possible to recommend the given system for growing coarse single crystals of diamond, since the probability of formation of a nucleus is relatively low in this case.

Comparison of our data with the the results of wetting of graphite and diamond by Ni–B and Ni–C melts in [7] show that the addition of a small quantity of nonmetals — boron and carbon — to nickel appreciably lowers the work of adhesion of the melt to the solid phase. This conclusion is consistent with our data for additions of sulfur. One possible explanation for the results is the formation of complexes in the melt [8], leading to a sharp reduction in the thermodynamic activity of nickel.

Thus, a eutectic nickel–sulfur melt weakly wets solids with either covalent or ionic chemical bonds. Adhesion work increases slightly with an increase in temperature. The interaction at the solid-liquid phase boundary is likely to be determined by physical forces, and only in the system ZnSe₃—(Ni–S)₉ can chemical reactions occur at the interface.

REFERENCES