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Wetting of nickel by silver

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Sessile drop experiments of molten silver and nickel were performed in air and helium at 970° C. A NiO layer formed at the interface in air; silver formed a 90° contact angle. In helium silver formed a 9° contact angle on nickel. The role of solution reactions in forming these angles is discussed.

1. Introduction

Wetting behaviour studies through sessile drop experiments is an important method of studying interfaces. particularly at pressures above vacuum. Earlier studies have shown that the Ag–Ni composite system is a potentially economic thick film system [1]. In this communication wetting behaviour of silver on nickel is studied and analysed.

Contact angles of silver on nickel were measured in air and gettered helium atmospheres. Spheres (0.0015 m diameter) of 99.99% pure silver were used, and the nickel substrates were polished before the experiment to remove any visible oxide layer and to obtain a flat surface. To study the interface, the specimen (silver drop on nickel substrate), after the wetting experiment, was sectioned perpendicular to the substrate at the centre of the drop using a diamond saw. One half was mounted in Bakelite, polished by standard metallographic techniques and examined using scanning electron microscopy (SEM) with attached energy dispersive X-ray analysis (EDAX) capability.

Under air-atmosphere conditions the silver sessile drop on a nickel substrate had a steady-state contact angle of 90° at 970° C. On melting, the silver drop had an initial obtuse contact angle and the steady-state angle of 90° was attained in less than five minutes. The surface of the substrate was tarnished, the drop was regular and the edge was regular. The adherence between the drop and the substrate was good. The cross-section of the interface as seen in SEM is shown in Fig. 1. X-ray line mappings of silver and nickel are also shown across the micrograph. A nickel oxide layer forms on the surface of nickel during temperature increase, before the silver melts, and remains between the nickel and the silver. The thickness of this layer as seen from the micrograph is about 5 to 6 μm. Slight solution of NiO in silver is noticeable by EDAX.

In a gettered helium atmosphere, at 970° C, an equilibrium contact angle of 9° was obtained in 30 min. The surface of the substrate was shiny, the drop shape was regular but the three-phase junction was irregular. There was strong adherence between the drop and the substrate. The scanning electron micrograph of the cross-section of the interface along with the X-ray line mappings of the nickel and the silver is shown in Fig. 2. Diffusion of nickel into silver and some silver into nickel can be noticed in this micrograph.

Reported surface energies of silver and nickel at 1000° C are given in Table I. Surface energy (γ_{sv}) of NiO is given as 400 mJ m^{-2}. The surface energy of solid silver is reported by Buttner *et al.* [6] to be sensitive to the presence of oxygen (Fig. 3). In an air atmosphere the surface energy of silver at 932° C is decreased to about 450 mJ m^{-2}, and in a helium atmosphere γ_{sv} is 1140 mJ m^{-2}. For liquid silver at 970° C, however, no such data was found, but it is logical to expect that γ_{lv} also is correspondingly lower in an air atmosphere.

From the 9° contact angle in a helium atmosphere, the driving force for wetting ($\gamma_{sv} - \gamma_{sl}$) could be calculated using Young's equation and assuming that the surface energies are as given in Table I; the value is 909 mJ m^{-2}. The calculated value of γ_{sl} then is 1311 mJ m^{-2}. In this case γ_{sv} for nickel is greater than γ_{lv} for silver. Strong adherence occurs because of the attainment of

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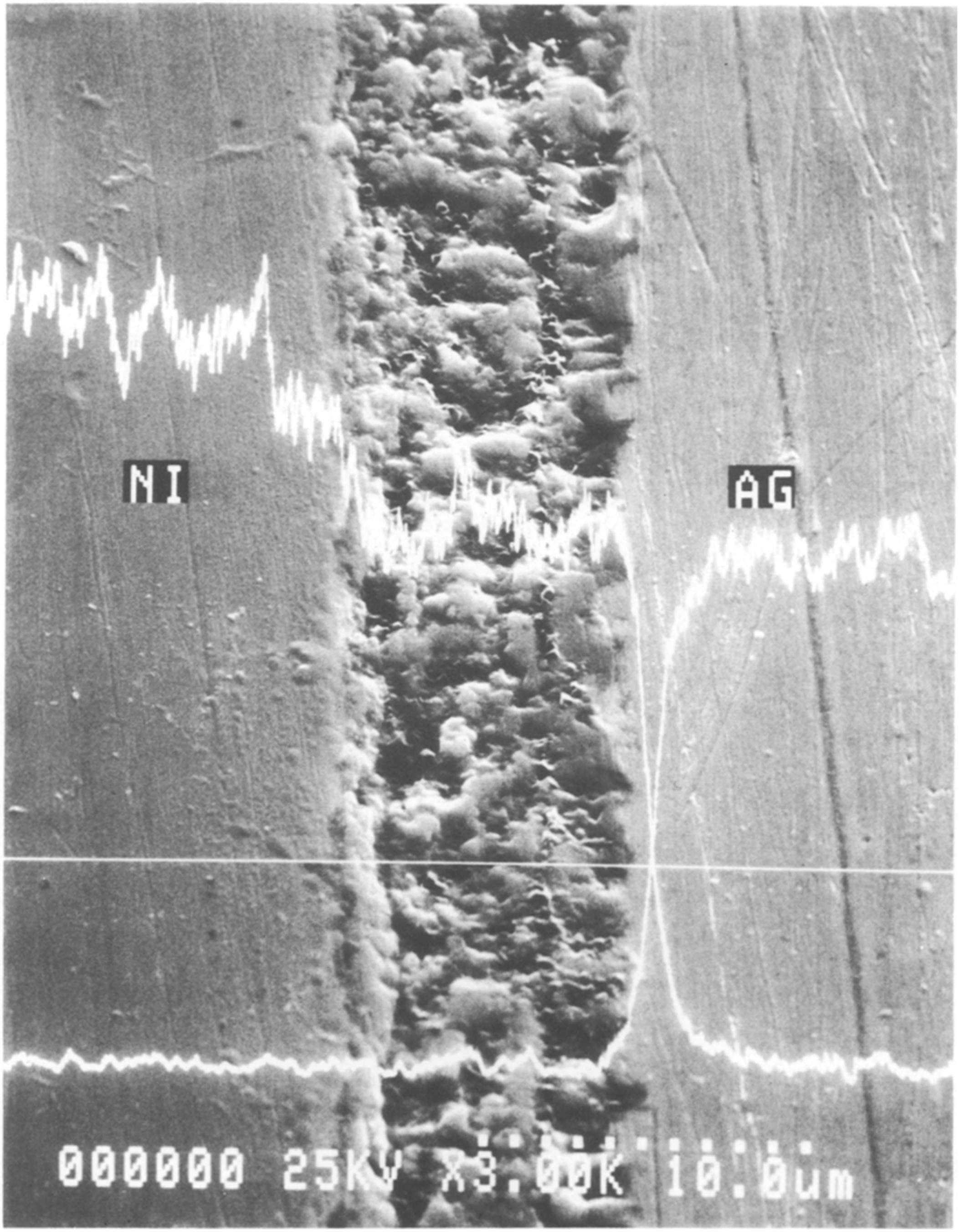

Figure 1 Cross-section of silver sessile drop on nickel in air at 970° C showing presence of NiO layer at interface. EDAX traces of nickel and silver along white horizontal line. (The overall extent of the dots represents 10 μm.)

thermodynamic equilibrium compositions in the interfacial zone, i.e. nickel is saturated with silver and silver with nickel.

In an air atmosphere the contact angle obtained (90°) is actually the contact angle between silver and the nickel oxide layer as evidenced from the scanning electron micrograph (Fig. 1). The step observed for the nickel intensity profile in the interface layer is due to the dilution of nickel by oxygen atoms to form NiO and thus is an indirect proof that the intermediate layer is nickel oxide. Across the NiO–Ag interface, the nickel intensity

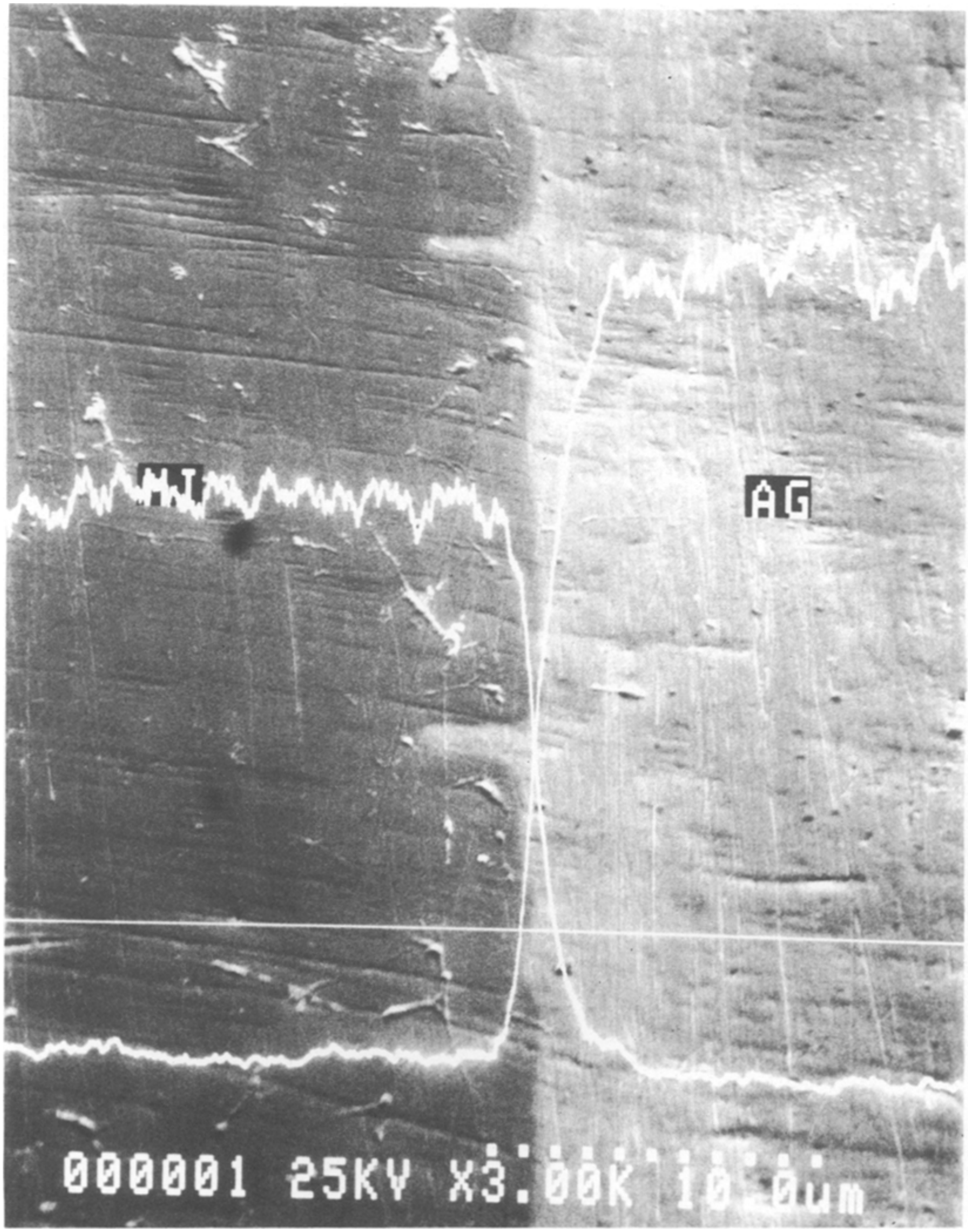

Figure 2 Cross-section of silver sessile drop on nickel in helium at 970° C. EDAX traces of nickel and silver along white horizontal line. (The overall extent of the dots represents 10 μm.)

decreases slowly reaching zero at about 3 μm into the silver region. This strongly indicates that NiO is slightly soluble in silver even though nickel is barely soluble in silver. Good adherence of NiO–Ag supports the existence of chemical bonds across the interface which have resulted because of this solution of NiO in silver leading to chemical equilibrium compositions at the interface.

To explain the 90° contact angle observed in this system, it is necessary to understand the thermodynamics and mechanics of wetting and spreading.

TABLE I Surface energies

Material	Melting point (°C)	Temperature (°C)	Surface energy (mJ m^{-2})	Reference
Silver	963	1000	920	[2]
Nickel	1453	1000	2280	[3]
			2160*	[4]
Nickel oxide	1957	1000	400	[5]

*Value approximated from liquid surface tension.

2. Analysis

Let us consider a solid–solid–vapour system wherein a small spherical liquid drop is placed on a flat, rigid, solid surface. The solid–liquid interface will form and continue to increase in area ($dA_{\rm sl}$) as long as the free energy change (δG) for the system remains negative. Assuming negligible gravitational effects and taking into account possible changes in the energies of the solid–vapour, liquid–vapour and solid–liquid interfaces, the free energy change for the system could be written as

$$\delta G = \delta \int_{\rm sl} d(\gamma_{\rm sl}A_{\rm sl}) + \delta \int_{\rm sv} d(\gamma_{\rm sv}A_{\rm sv}) + \delta \int_{\rm lv} d(\gamma_{\rm lv}A_{\rm lv}). \qquad (1)$$

The interfacial areas determine the contact angle (θ) at the three-phase junction point and the height of the drop, h, shown in Fig. 4, as determined by Aksay *et al.* [7]. Several progressive configurations of the drop and corresponding changes in the areas of the liquid–vapour and solid–liquid interfaces against the contact angle (or the height of the drop h) are shown in the figure.

Equation 1 can be written as

$$\frac{dG}{dh} = \frac{d(\gamma_{\rm sl}A_{\rm sl})}{dh} + \frac{d(\gamma_{\rm sv}A_{\rm sv})}{dh} + \frac{d(\gamma_{\rm lv}A_{\rm lv})}{dh}. \qquad (2)$$

Let us consider the sign of decreasing height to be positive. Expanding Equation 2

$$\frac{dG}{dh} = \gamma_{\rm sl}\frac{dA_{\rm sl}}{dh} + A_{\rm sl}\frac{d\gamma_{\rm sl}}{dh} + \gamma_{\rm sv}\frac{dA_{\rm sv}}{dh} + A_{\rm sv}\frac{d\gamma_{\rm sv}}{dh} + \gamma_{\rm lv}\frac{dA_{\rm lv}}{dh} + A_{\rm lv}\frac{d\gamma_{\rm lv}}{dh}. \qquad (3)$$

Values for both $\gamma_{\rm lv}$ and $\gamma_{\rm sv}$ are dependent on the atmosphere. Since the atmosphere would remain constant throughout an experiment and the solid and liquid normally rapidly reach equilibrium with the vapour phase independently of each other, the variation of $\gamma_{\rm sv}$ and $\gamma_{\rm lv}$ with time would be negligible, i.e. $d\gamma_{\rm sv}/dh$, $d\gamma_{\rm lv}/dh$ would be zero. Equation 3 then becomes,

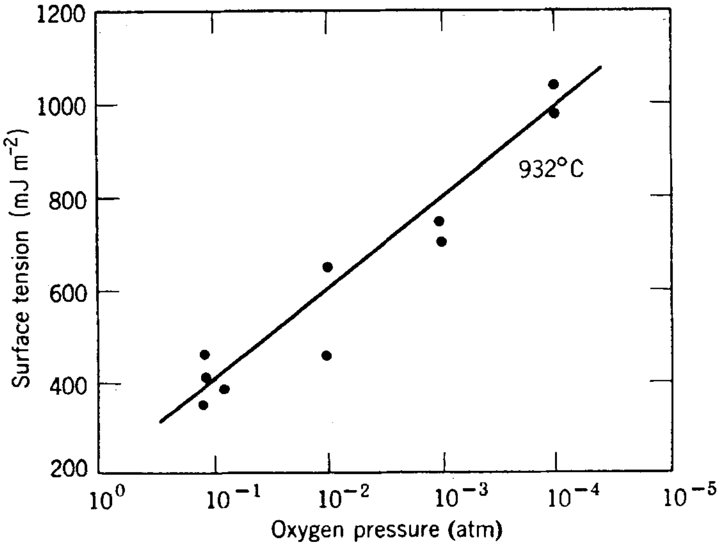

Figure 3 Effect of oxygen pressure on surface tension of solid silver at 932°C (Buttner *et al.* [6]).

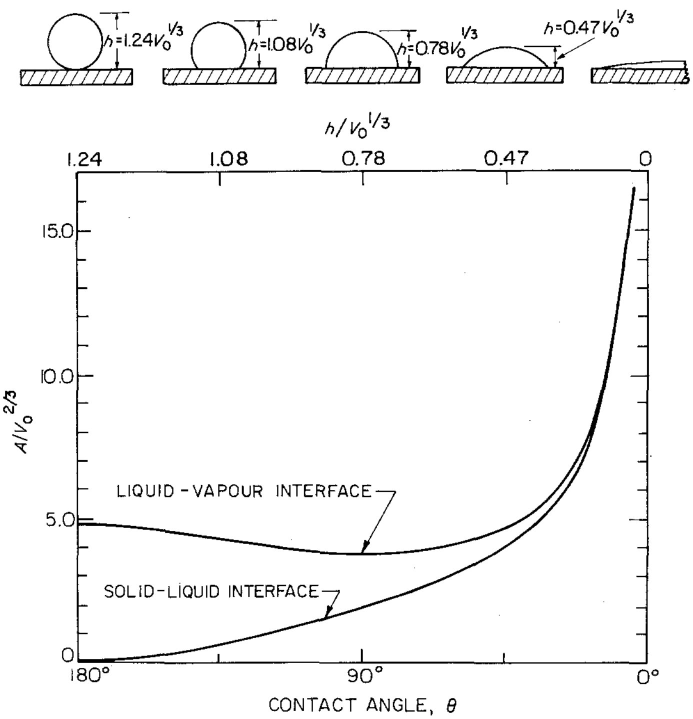

Figure 4 Interfacial areas as a function of contact angle of sessile drop (Aksay *et al.* [7]).

$$\frac{dG}{dh} = \gamma_{sl}\frac{dA_{sl}}{dh} + A_{sl}\frac{d\gamma_{sl}}{dh} + \gamma_{sv}\frac{dA_{sv}}{dh} + \gamma_{lv}\frac{dA_{lv}}{dh}. \qquad (5)$$

If there is a reaction between the solid and liquid phases, the γ_{sl} will continuously change until equilibrium is reached. The change of γ_{sl} is negative causing a decrease in the contact angle and the height of the drop to satisfy the balance of forces. Furthermore, $dA_{sl} = -dA_{sv}$ as the liquid–solid interface is formed. Equation 4 then becomes

$$\frac{dG}{dh} = (\gamma_{sl} - \gamma_{sv})\frac{dA_{sl}}{dh} + \gamma_{lv}\frac{dA_{lv}}{dh} + A_{sl}\frac{d\gamma_{sl}}{dh}. \qquad (5)$$

This expression represents the variation of free energy with the height of the drop, and thus the contact angle, for non-equilibrium conditions where the reaction at the solid–liquid interface is still proceeding. As the reaction proceeds, h keeps decreasing (hence positive according to the sign convention) and γ_{sl} also keeps decreasing (negative). When the reaction is over, γ_{sl} reaches a constant equilibrium value making $d\gamma_{sl}/dh = 0$. Equation 5 is then reduced to Equation 6 which was derived by Aksay *et al.* [7]. With constant interfacial energies

$$\frac{dG}{dh} = (\gamma_{sl} - \gamma_{sv})\frac{dA_{sl}}{dh} + \gamma_{lv}\frac{dA_{lv}}{dh} \qquad (6)$$

an equilibrium configuration is reached when A_{sl} and A_{lv} reach values that result in $dG/dh = 0$.

If $\gamma_{sv} < \gamma_{sl} < \gamma_{lv}$, then the contact angle will be obtuse because dA_{sl} is positive and dA_{lv} is negative (Fig. 4) on a change of θ from 180° to 90°. Under chemical equilibrium conditions, the formation of a true interface could be considered analogous to the formation of a solution involving an adjustment of surface structures to form an intermediate interfacial structure (with an interfacial tension between that of γ_{sv} and γ_{lv}). The actual magnitude of γ_{sl}, however, depends on the degree of chemical bonding or minimization of structural discontinuity across the interface developed in the system. γ_{sl} becomes smaller with increased chemical bonding.

In the present case $\gamma_{lv} > \gamma_{sv}$, i.e. the surface energy of liquid silver is greater than that of NiO, and an obtuse angle is obtained initially. With solution of NiO by the silver, the surface energy of the silver is reduced by the reaction causing γ_{ls} to be reduced resulting in a decrease of θ. However, γ_{sl} can not be reduced relative to γ_{sv} because no silver is dissolved in NiO; γ_{sl} thus decreases until it is equal to γ_{sv}. The first term in Equation 6 then becomes zero and the equation is reduced to Equation 7.

$$\frac{dG}{dh} = \gamma_{lv}\frac{dA_{lv}}{dh}. \quad (7)$$

According to this equation the equilibrium configuration is reached when $dG = 0$. As the contact angle decreases to 90°, dA_{lv} is negative as seen in Fig. 4. With any further decrease in the contact angle beyond 90°, dA_{lv} in Equation 6 would be positive (Fig. 4) which would make dG positive which is thermodynamically forbidden. The silver drop thus reaches an equilibrium contact angle of 90° since γ_{sv} is not reduced by the silver. This corresponds to the spreading of a drop whose $\gamma_{lv} > \gamma_{sv}$ in the presence of a reaction in which the solid is the passive participant.

3. Conclusions

Silver wetted nickel in helium atmosphere (contact angle 9°). The reduction of γ_{sl} due to the contribution of the solution reaction in which the solid was an active participant (solution of silver by nickel) caused a reduction in the contact angle θ, but the contribution of the free energy of the reaction was not large enough to cause a sufficient increase in the driving force for wetting to result in spreading of the liquid.

In an air atmosphere a nickel oxide layer formed before the silver melted and remained between the nickel and silver; a steady-state contact angle of 90° was obtained since the surface energy of silver (γ_{lv}) is greater than the surface energy of NiO (γ_{sv}) and no silver dissolved in the NiO. As an equilibrium composition interface developed by solution of NiO into the silver, γ_{sl} was continuously reduced until it was equal to γ_{sv} resulting in the 90° angle according to Young's equation. This condition corresponds to the spreading of a liquid, whose $\gamma_{lv} > \gamma_{sv}$, due to a reaction in which the solid is a passive participant. If the solid was an active participant in the reaction, actual spreading would have occurred, i.e. the contact angle would have continued to decrease. Good adherence was realized in both cases because of the development of thermodynamic equilibrium compositions in the interfacial zones.

References

1. V. K. NAGESH and J. A. PASK, *Int. J. Hybrid Microelectronics* 4 (1981) 65.
2. W. D. KINGERY, "Introduction to Ceramics", 2nd edn (John Wiley and Sons, New York, 1976) p. 183.
3. B. C. ALLEN, in "Liquid Metals", edited by Sylvan Z. Beer (Marcel Dekker, New York, 1972) Chap. 4, p. 198.
4. L. E. MURR, "Interfacial Phenomena in Metals and Alloys" (Addison Wesley, Reading, Massachusetts, 1975) p. 123.
5. A. A. APPEN, "High Temperature Inorganic Coatings" (WNT Warsaw, Warsaw, 1970) p. 49 (translated from Russian).
6. F. H. BUTTNER, E. R. FUNK and H. UDIN, *J. Phys. Chem.* 56 (1952) 657.
7. I. A. AKSAY, C. E. HOGE and J. A. PASK, *ibid.* 78 (1974) 1178.

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