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Wettability and spreading kinetics of liquid aluminium on boron nitride

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The wettability and spreading kinetics of liquid Al on CVD-BN were investigated by the sessile drop method in a vacuum of about 1.1×10^{-3} Pa at 1070 to 1430 K. The wettability on the Al–BN system was different from that of the Al–SiC system reported in the literature. The wetting angle of Al–BN linearly decreased with an increase of temperature in high temperature range, and tended towards 15° at 1430 K. Complete wetting could be obtained at about 1470 K. The interface energy between liquid Al and the reaction layer and the surface energy of CVD-BN were calculated by means of Warren thermodynamics analysis. The surface of CVD-BN was examined by XRD. The results show that the surface of CVD-BN was chiefly composed of those low energy planes parallel to (001). According to the relationship of the spreading kinetics from the experiments, the apparent activation energy of the liquid Al spreading on the surface of CVD-BN was calculated. The result shows that the activation energy of interfacial reaction accounts for about 54% of the spread activation energy. The spread of liquid Al on CVD-BN was affected by the interfacial reaction, diffusion and liquid movement on the surface.

1. Introduction

High purity chemical vapour deposition (CVD) boron nitride is one of the ceramic nitrides that have high chemical stability and high-temperature strength. It is used as a refractory for melting high pure alloy, crystal growth and the special nozzle. Since the boron nitride possesses a high thermal transmittance and a high insulance, it would be used in the electronics industry as radiator substrate in large amounts. The composite production and joining of boron nitride to metal is of great interest to the researchers.

Research on the wettability and spreading kinetics of liquid metal on the surface of ceramic will help to understand the reaction between metal melt and refractory and the features of the metal–ceramic interface, moreover, to promote the composite production and the design of metal filler for the metal–ceramic joints.

Previous studies on the wettability for Al–ceramics showed that for Al–SiC system and Al–Al_2O_3 system, the wetting of ceramics by liquid Al was controlled by a liquid phase interface formed by an ordinary dissolving reaction: SiC and Al_2O_3 dissolving into aluminium [1, 2]. Very little research has been done on the wettability for Al–ceramic system for which no liquid phase interface exists. At present, there is no systematic report on the wettability and the spreading kinetics of liquid Al on the surface of BN.

To understand the law of the wetting and spreading kinetics of Al–ceramic system where there is no solubility between Al and ceramic, but exists a stable reaction interface, we carried out this work. The spread rate constant was defined by the spread experiments, and the apparent activation energy on the spreading kinetics process was calculated.

2. Experimental procedure

2.1. Materials and method

The purity of the aluminium employed was 99.999%. The sample weight was approximately 25 mg. The chemical vapour deposit boron nitride (over 99.99% purity), CVD-BN, was used as the solid substrate. The CVD-BN substrate is a disc of 15 mm diameter and 0.3 mm thickness. The surface of the substrate was polished with 0.5 μm diamond and 0.05 μm SiC powder, respectively, and both the substrate and the Al sample were cleaned by ultrasonic agitation in acetone for 20 min before experiment.

The sessile drop method was used to study the wettability and spreading kinetics of the CVD-BN by liquid Al. The apparatus and the measurement methods used for this work are quite similar to those of our earlier reports [3, 4].

In order to avoid the sample being oxidized, the experiments were carried out in a vacuum, and a vacuum sample conveyer was employed to prevent the gas absorbed in the system contaminating the metal melt in the experiment process. The Al sample was placed in the tail of the channelled-Mo of the vacuum sample conveyer before heating. After the vacuum reached 1.1×10^{-3} Pa, high purity argon (over 99.999%) flowed into the furnace for at least 30 min. The chamber of the furnace was then evacuated. When

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the vacuum reached 1.1×10^{-3} Pa again, the experiment was carried out according to the following procedure.

(1) To eliminate the gas absorbed in the system, the temperature was held for 30 min at 100 K above the experiment temperature, during which the highest temperature of the sample in the vacuum sample conveyer was about 400 K.

(2) The sample was conveyed onto the CVD-BN substrate at the specific experiment temperature.

(3) After the sample had melted completely, the timing began and photographs were taken at various time intervals.

To purge the atmosphere as much as possible, Zr–10RE alloy shot (RE: rare earth, about Ce 50 wt %, La 25 wt %, Nd 16 wt %, Pr 6 wt %) was placed round the substrate. The oxygen partial pressure estimated around the sample in the experimental process was lower than 10^{-15} Pa.

The dimensions required for the calculations of the wetting angle and spread ratio were taken from the photographs measured by a projector. The surface composition of CVD-BN was examined by means of XRD.

2.2. Definition of spread ratio, α

The sessile drop method is an effective method to investigate the wetting and spreading between liquid and solid. Much helpful information can be obtained from it, such as the surface tension of liquid phase, wetting angle of liquid–solid and the spread area. In previous studies on spreading kinetics, the spread area per unit weight was measured as an object of study. This treatment would result in differences in the various spread area per unit weight in the same system, because of the different weights taken. For example, supposing the liquid drop is spheric cap, two drops 1 and 2 possess the same density (ρ), the volume ratio of the two droplets is ω, i.e. $V_1/V_2 = \omega$, if the wetting angle (θ) of them with the solid substrates are alike, the two spread areas per unit weight are given by $S'_1 = \pi R_1^2 \sin^2\theta / V_1 \rho^{-1}$ and $S'_2 = \pi R_2^2 \sin^2\theta / V_2 \rho^{-1}$, respectively, here R_1 and R_2 are the principal radii of the two spheric caps, respectively. Then $S'_1/S'_2 = \omega^{-1/3}$, therefore the volume of the liquid drop is larger and the spread area per unit weight is smaller.

To let the experimental values of the various volume drops be comparable with each other and have no effect on the law of the spreading kinetics, we take the ratio of the spreading area (S) in the experimental process to the intrinsic cover area (S_0) of the drop (the equatorial plane of liquid drop when $\theta = 180°$) as the spread ratio (α) of liquid on solid. As above, the two intrinsic cover areas are given by $S_{01} = \pi R_{10}^2$ and $S_{02} = \pi R_{20}^2$, then $S_{01}/S_{02} = \omega^{2/3}$. When the two wetting angles are the same, the spreading areas of 1 and 2 are given by $S_1 = \pi R_1^2 \sin^2\theta$ and $S_2 = \pi R_2^2 \sin^2\theta$, then $\alpha_1/\alpha_2 = S_1 S_2^{-1} / S_{01} S_{02}^{-1} = \omega^{2/3}\omega^{-2/3} = 1$, therefore the spread ratio α of various weight sample is the same for the same system and experimental conditions. In this paper, the kinetic relationship of the spread ratio (α) of the Al–BN system with the reaction time was investigated.

3. Result and discussion

3.1. Wettability

In the present study, a typical example of holding time dependence of the wetting angle (θ) on Al–CVD-BN system is shown in Fig. 1. The relation curve of θ against t at 1190 K is composed of three stages: incubation, quasi-steady decrease and trend constant. The experimental temperature is lower, the first and second stages are longer. The wetting angle held constant at 1070 K, and no second and third stages were observed during the experiment. When the temperature was 1380 K, the incubation vanished, and θ decreased at a large slope during the initial reaction. The wetting angle scatter in the experiment error after a reaction time of 3.6 ks.

Fig. 2 shows the isochrones of temperature dependence of the wetting angle between Al and CVD-BN. There are three temperature ranges of the wetting angle change on the 1.8 and 3.6 ks isochrones. From 1070 to about 1200 K, the wetting angle decreased at a slower rate with an increase of the temperature. The absence of solubility between Al and BN, means that it could be deduced that the chemical reaction of Al–BN

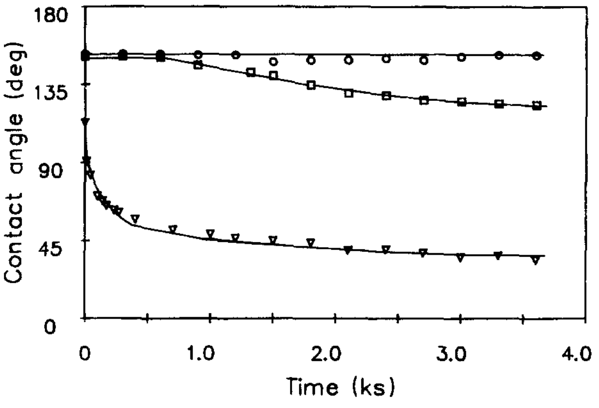

Figure 1 Variation of wetting angle θ with time t for liquid aluminium on CVD-BN at various temperatures (○ 1070 K, □ 1190 K, ▽ 1380 K).

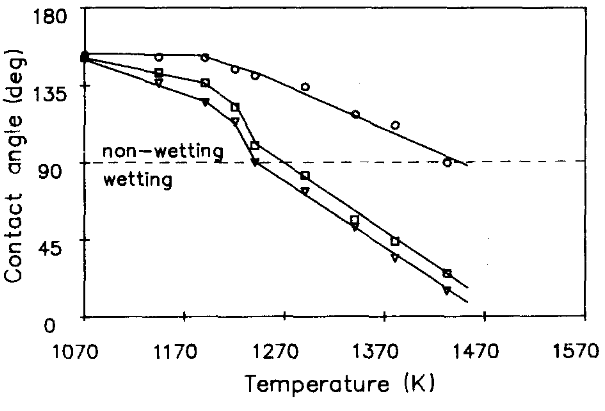

Figure 2 Isochrones of temperature dependence of the wetting angle θ between aluminium and CVD-BN (○ 0 ks, □ 1.8 ks, ▽ 3.6 ks)

existed in this temperature range. The weak chemical reaction resulted in a small change of wetting angle due to the low temperature. In this range, the equilibrium oxygen partial pressure of Al–Al_2O_3 of about 10^{-42} to 10^{-33} Pa and the vapour pressure of aluminium are low, therefore the oxide film on the surface of the liquid aluminium could not be dispelled completely in the experimental process. A larger wetting angle of Al/CVD-BN, $\theta > 120°$, thus resulted in this temperature range.

In the 1200 to 1250 K temperature range, the wetting angle acceleratively decreased as the temperature rose, and the transition of "non-wetting ($\theta > 90°$) to wetting ($\theta < 90°$)" was observed on the 3.6 ks isochrone. It is reasonable to presume that since the high vapour pressure ($> 10^{-1}$ Pa) of aluminium, the liquid Al surface vaporization gradually dispelled the retardation of oxide film to the wetting in this system. When the temperature was higher than 1250 K, the wetting angle decreased at a large slope with an increase of temperature. On the 3.6 ks isochrone, the wetting angle tended toward 15° at 1430 K. From the tendency of wetting angle change, the equilibrium wetting angle could reach 0° at 1470 K.

In the relationship of temperature dependence of wetting angle of Al–SiC system, as shown in Fig. 3 [2, 5], the wetting angle tends to a constant in the high temperature range. On the 1.8 ks isochrone, the constant wetting angle of Al–SiC is about 38°. In the present study on the Al–CVD-BN system, however, the wetting angle decreased rapidly as the temperature rose in the high temperature range. When the experimental temperature was lower than 1380 K, the wetting angle values of Al–SiC were less than our measurement on Al–CVD-BN. We think that these observed differences are due to the difference in the interface formed features for both Al–SiC and Al–BN. For Al–SiC system, a dissolving reaction of SiC dissolving into aluminium can occur at 923 K [6] and the solubility of Si in liquid Al is large. After the surface layer of SiC decomposed in liquid Al, the formation at the liquid interface of Al–Si solution resulted in that the formation of the stable compact Al_4C_3 layer being very difficult in this interface. The transition of "non-wetting–wetting" in Al–SiC system could occur at a lower temperature after the retardation of oxide film to wetting dispelled. Since the saturation of SiC in the liquid, the wetting angle of the Al–SiC system tended to a constant in the high temperature range [2].

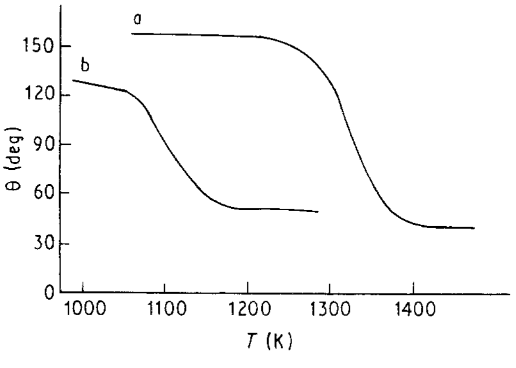

Figure 3 Isochrones of temperature dependence of the wetting angle θ between aluminium and SiC in reaction time 1.8 ks (a according to Köhler [5], $P = 2$ to 8×10^{-4} Pa, b according to Laurent [2], $P = 10^{-4}$ to 5×10^{-5} Pa and $P_{O_2} = 10^{-16}$ Pa)

For the Al–BN system, there is no solubility between aluminium and BN, therefore the formation of the interface is determined by the chemical reaction with each other. In the study of EPMA and XRD for the interface of Al–HP-BN and Al–CVD-BN, we noted that a stable interfacial reaction layer formed of AlN and aluminium boride, between liquid aluminium and boron nitride [7, 8]. The reaction layer retarded the further reaction between liquid aluminium and boron nitride, so the temperature of the "non-wetting–wetting" transition of Al–BN is higher than that of Al–SiC. In the high temperature range, since the interfacial reaction and the diffusion of Al in the interface layer rose with an increase of temperature and a little AlN dissolved into liquid Al [9], the wetting angle could decrease rapidly as the temperature rose. The complete wetting state could thus be obtained at 1470 K.

3.2. Interfacial energy and surface energy

Since a stable interface formed in the Al–BN system and there existed a layer of AlN on the bottom of liquid Al drop [7, 8], when the system reached thermodynamic equilibrium, i.e. the wetting angle constant, the surface energy of liquid Al ($\gamma_{lv(Al)}$), the surface energy of solid BN ($\gamma_{s(BN)}$) and the interfacial energy of liquid Al–solid AlN ($\gamma_{sl(Al/AlN)}$) could be given by Young's equation as follows

$$\gamma_{s(BN)} = \gamma_{sl(Al/AlN)} + \gamma_{lv(Al)} \cos\theta \qquad (1)$$

As soon as the interfacial energy $\gamma_{sl(Al/AlN)}$ is estimated, the surface energy of BN $\gamma_{s(BN)}$ can be calculated using Equation 1.

Using Warren thermodynamic analysis [10], the interfacial energy in binary system can be written as

$$\gamma_{sl} = \gamma'_{sl} + \gamma''_{sl} \qquad (2)$$

where γ'_{sl} is the energy of a solid–liquid interface between a solid and a liquid with the same composition. γ''_{sl} is the energy of a solid–liquid interface between two structurally similar but chemically different phases. For the interface of the pseudo-binary systems of no liquid dissolving into the solid, according to Warren's two atomic layers interface thermodynamic model, γ'_{sl} and γ''_{sl} are given by

$$\gamma'_{sl} = kT_m/b(V/b)^{2/3} \qquad (3)$$

$$\gamma''_{sl} = nF/N \qquad (4)$$

$$\begin{aligned} F = {} & H_m(1 - T/T_m)X^2 + RT[X\ln X \\ & + (1 - X)\ln(1 - X)] - RT\ln X_s \\ & \times [X(1 - X)] \end{aligned} \qquad (5)$$

$$X = (n_l X_s + n_s)/n \qquad (6)$$

where T_m is the melting point of solid (K), b the number of atoms in the solid molecule, V the molar volume of the compound solid (m^3), n the number of

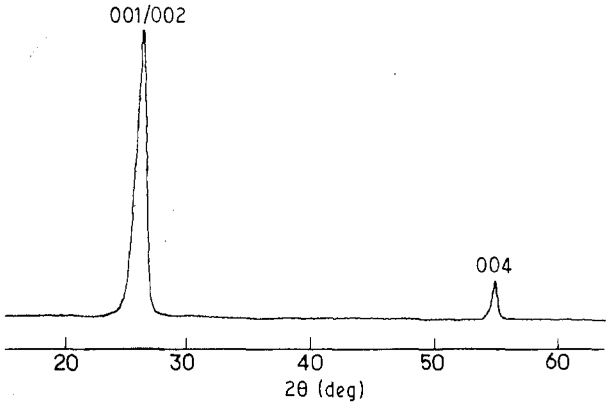

Figure 4 The X-ray diffraction pattern from CuK_α radiation for the surface of CVD-BN substrate.

interface atoms, $n_s + n_l$, k an empirical constant, between 5×10^{-4} and 8×10^{-4} [11], H_m the latent heat of melting of solid, X_s the molar fraction of solid atoms in liquid solution and N Avogadro's number.

The molar fraction of solid AlN in liquid Al solution is very small. The estimated value of X_s is about 10^{-2} at 1380 K [9]. For this system the value of γ_{sl} was estimated using Equations 2 to 6 with the values of $k = 6.5 \times 10^{-4}$ and $X_s = 10^{-2}$. The value of the interfacial energy of liquid Al with solid AlN γ_{sl} is approximately 0.410 J m^{-2}. According to the relationship of θ–t in this experiment, the equilibrium wetting angle at 1380 K is close to 35°. The surface energy of liquid Al at 1380 K was taken from [7], $\gamma_{lv(Al)} = 0.760$ J m^{-2}. Recalling Equation 1 and combining it with above parameters, the value of surface energy of CVD-BN is approximately 1.03 J m^{-2}.

The XRD analysis of the CVD-BN substrate showed that the surface of it was chiefly composed of the strong plane (0 0 1), as shown in Fig. 4. From a knowledge of the relationship between crystal planes and surface energy, we know that the strong plane possesses a low surface energy. On measurement of the surface energy of various planes in the graphite crystal, the surface energy of the strong plane (0 0 1) was estimated to be about 0.990 J m^{-2} at 1380 K [12]. Considering that the crystal structure of CVD-BN is similar to that of graphite and the chemical bond energy of B–N (385 kJ mol^{-1} [13]) is close to that of C–C (348 kJ mol^{-1} [13]), we estimate that the surface energy of the strong plane (0 0 1) in CVD-BN crystal is approximately 0.90 to 1.00 J m^{-2}.

3.3. Spreading kinetics

The results of the spread experiment for liquid aluminium on the CVD-BN substrate are shown in Fig. 5. There was an incubation at low temperature. Above 1220 K the incubation vanishes and the relationship between spread ratio α and spread time t is close to the exponential function. The spread of liquid drop on the solid decelerated, and the spread ratio tended to a constant with an elapsing time.

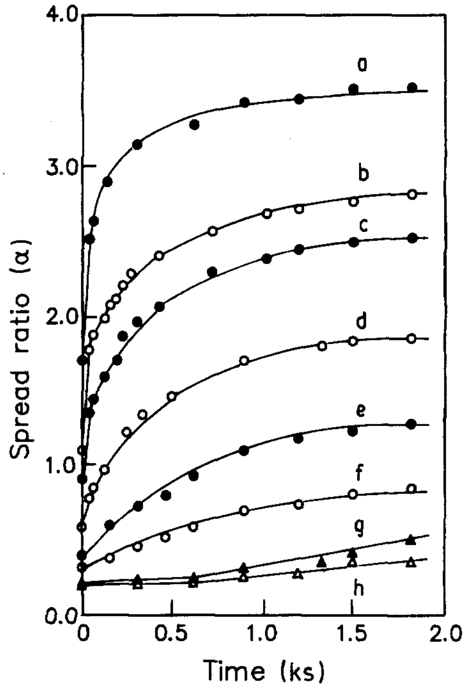

Figure 5 Spread time t dependence of spread ratio α for liquid aluminium on CVD-BN at various temperatures (a 1430 K, b 1380 K, c 1340 K, d 1290 K, e 1240 K, f 1220 K, g 1190 K, h 1140 K).

A plot of $\ln(\alpha - \alpha_0)$ against $\ln(t - \tau)$ at various temperatures, gave approximately straight lines in an elapsed time 1.2 ks, as shown in Fig. 6. The linear ranges are the so-called "quasi-steady spread range" [14]. The spread ratio of the liquid aluminium with the spread time in this range can be given by

$$(\alpha - \alpha_0)^{1/n} = k(t - \tau) \qquad (7)$$

where α_0 is the spread ratio at $t = 0$, t the spread time (s), τ the incubation (s), k the spreading rate constant

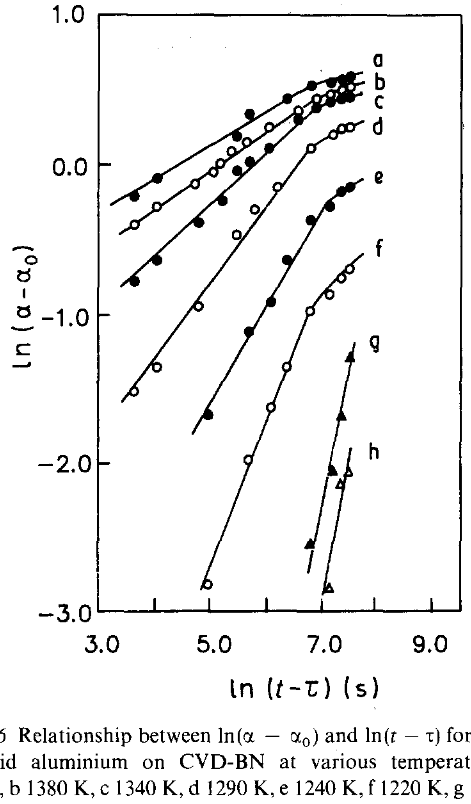

Figure 6 Relationship between $\ln(\alpha - \alpha_0)$ and $\ln(t - \tau)$ for spread of liquid aluminium on CVD-BN at various temperatures (a 1430 K, b 1380 K, c 1340 K, d 1290 K, e 1240 K, f 1220 K, g 1190 K, h 1140 K).

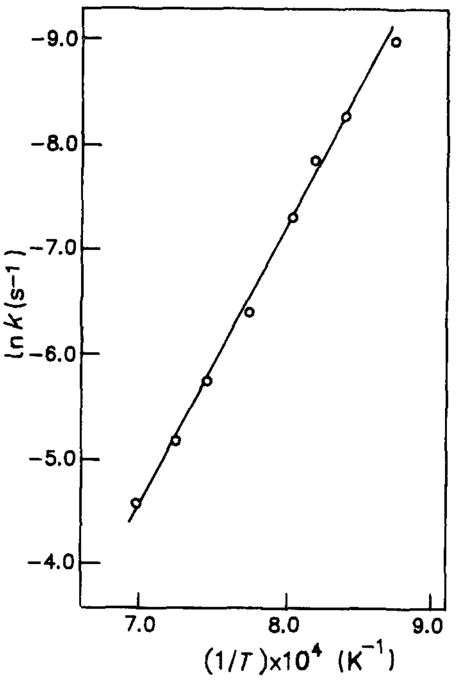

Figure 7 Variation of ln of spread rate constant k with inverse of temperature T for spread of liquid aluminium on CVD-BN.

(s^{-1}) and n the spread index, relating to the interfraction within the liquid phase and between liquid drop and interface.

Following the example of the treatment method of chemical reaction kinetics, plots of $\ln k$ against $1/T$, where T is the temperature in K, as shown in Fig. 7. From this figure, the plot of $\ln k$ against $1/T$ is a straight line, and follows Arrhenius behaviour. Hence, the value of the apparent spread activation energy Q could be calculated from the straight line, about 216 kJ mol^{-1}.

The liquid metal spreading on the ceramic surface is chiefly affected by the interfacial chemical reaction, diffusion, ceramic dissolving into the liquid metal and the interfraction within liquid phase and between liquid drop and solid interface [15, 16]. Boron nitride does not dissolve into liquid aluminium, therefore the spreading process of liquid aluminium on its surface may be determined by the chemical reaction, diffusion and the interfraction. According to reaction kinetics theory, the activation energy for BN decomposing under the action of Al is about 30% of the energy of B–N bond (385 kJ mol^{-1} [13]). The reaction activation energy of the Al–BN system is approximately 116 kJ mol^{-1} hence only accounts for about 54% of the spread activation energy calculated by this study. The surplus 46% could be the activation energy for aluminium diffusion in the interface and liquid movement on solid.

References

1. J. J. BRENNAN and J. G. EBERHART, *J. Amer. Ceram. Soc.* **51** (1968) 569.
2. V. LAURENT, D. CHATAIN and N. EUSTATHOPANLOS, *J. Mater. Sci.* **22** (1987) 244.
3. J. T. WANG, M. S. BIAN and M. C. ZENG, *Acta Metall. Sinica* **17** (1981) 359.
4. M. S. BIAN, Q. CHEN and J. T. WANG, *ibid.* **24** (1988) B139.
5. W. KÖHLER, *Aluminium* **51** (1975) 443.
6. J. C. VIALA, P. FORTIER, C. BERNARD and J. BOUIX, "Developments in the Science and Technology of Composite Materials" (A. E. C. M., Bordeaux, 1985).
7. X. M. XUE, J. T. WANG and M. X. QUAN, *Mater. Sci. Eng.* **A132** (1991) 277.
8. X. M. XUE, J. T. WANG and F. M. ZHAO, *J. Mater. Sci. Lett.* accepted for publication.
9. H. A. WRIEDT, *Bull. Alloy Phase Diagr.* **7** (1986) 329.
10. R. WARREN, *J. Mater. Sci.* **15** (1980) 2489.
11. G. GRIMVALL and S. SJÖDIN, *Physica Scripta* **10** (1974) 340.
12. S. K. RHEE, *J. Amer. Ceram. Soc.* **55** (1972) 300.
13. H. B. GRAY, "Chemical Bonds" (Benjamin, New York, 1973).
14. E. D. SHUKIN, U. V. GORIUK'OV, G. I. DENISHIKOVA, N. V. LORCHOV and B. D. SUMM, *J. Colloid Russian* **25** (1963) 108.
15. Q. JIA and X. HU, in Proceedings of the 5th Symposium on the Physical Chemistry of Process Metallurgy, China Society Metals (Xian, 1984) 320.
16. J. V. NAIDICH, *Prog. Surf. Membr. Sci.* **55** (1981) 353.

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