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Interfacial reactions between SiC and aluminium during joining

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Reactions between SiC and liquid aluminium were studied. Transmission electron microscopy (TEM) showed that aluminium carbide (Al_4C_3) phase was formed at the interface between pressureless sintered SiC and aluminium. In contrast, the Al_4C_3 phase was not detected at the reaction sintered SiC–Al interface. This difference in microstructures results in the change in bending strength of the joints. Mixtures of SiC and aluminium powders were heated to react in vacuum in the temperature range 973 to 1473 K and the reaction products were examined using X-ray powder diffraction. It was confirmed that Al_4C_3 and silicon were formed, and that the extent of reaction between SiC and aluminium was decreased by the addition of silicon into aluminium.

1. Introduction

In accordance with the growing demand of ceramic materials in technological applications, the manufacturing and processing techniques of high performance ceramics have been developed for making precision parts. In such a case, it is important to establish joining techniques to form complex components. This paper deals with joining properties of SiC bodies and that of a SiC–Al composite, which is one of the important candidate materials for use in airplanes, automobiles and the first wall of fusion reactors.

We have reported a joining method of sintered bodies of SiC[1], in which aluminium plate of 0.5 mm thick was placed between two SiC bodies (10 mm x 10 mm x 15 mm) and joined in the temperature range 1073 to 1273 K in vacuum for a few minutes by induction heating. The measurements of 4-point bending strength of the joints were carried out from room temperature (RT) to 823 K in vacuum of about 10^{-2} Pa except at RT. The results for specimens which were joined at 1273 K are shown in Fig. 1. The 4-point bending strengths at RT were about 240 and 110 MN m^{-2} for the joints of pressureless sintered SiC and of reaction sintered SiC, respectively. This difference in joining strength is considered to be closely related with a reaction between SiC and aluminium.

In regard to the reaction between SiC and aluminium, the following reaction equation is usally considered,

$$3SiC(s) + 4Al(l) \rightarrow Al_4C_3(s) + 3Si(s) \qquad (1)$$

However, since the free energy change of this reaction is positive in the temperature range mentioned above, the reaction does not spontaneously proceed from the thermodynamic point of view. Clinton *et al.* [2] found a trace of reaction between REFEL SiC and aluminium at 1073 K. Kohara and Muto [3] examined the compatibility of SiC fibre with aluminium. In the latter experiment, the fibre specimens were aluminium-coated by vacuum evaporation and heat treated in air. The specimens showed noticeable degradation in tensile strength after the heat treatment at 973 K and the degradation was decreased by alloying silicon with aluminium.

In the present paper, studies were made of mechanisms for the joining of SiC and aluminium by microstructural observation of two kinds of sintered SiC–Al interface, and the effect of silicon on the reaction between SiC and aluminium was discussed.

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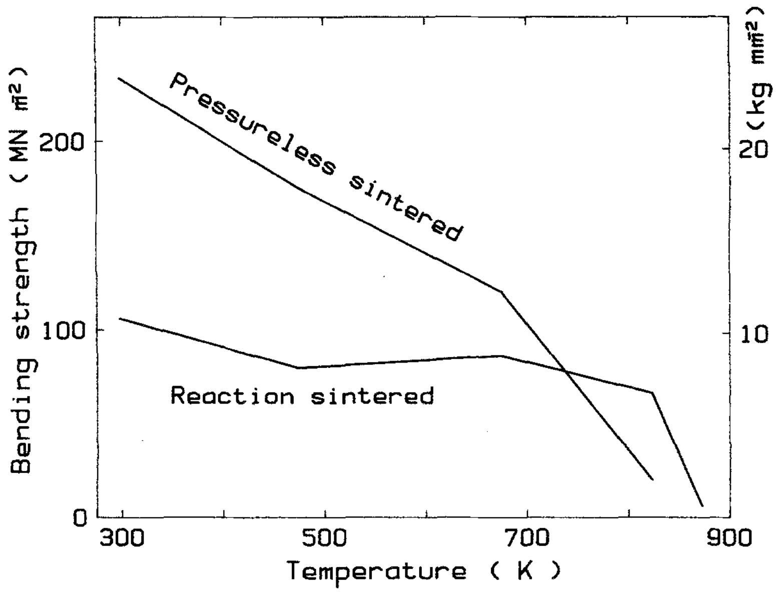

Figure 1 Strength in 4-point bending at high temperatures. Pressureless sintered and reaction sintered SiC were joined by liquid aluminium at 1273° C [1].

2. Experiments and results

2.1. TEM study of sintered SiC–Al interface

Pressureless sintered SiC (PLS SiC), SC 201, and reaction sintered SiC (RB SiC) were used to study the reaction between SiC and aluminium. The specimens were made by Kyocera Co., Ltd. and Shin-etsu Chemical Co., Ltd, respectively. The PLS SiC contains about 1 wt% B and C, and the RB SiC contains about 10 wt% free silicon and 0.05 wt% Fe. Aluminium metal (99.999% purity) was supplied by Osaka Asahi Metal Mfg. Co., Ltd.

The SiC–Al specimen for observation with transmission electron microscope (TEM) was prepared as follows. The sintered SiC was polished with 1 μm diamond paste and was washed with acetone. The surface of an aluminium metal block (1 mm x 1 mm x 1 mm) was also polished and washed with acteone. The sintered SiC and aluminium block were in contact with each other and were heat treated at 1373 K in a vacuum of 10^{-2} Pa for 1 h. Then the specimen was sliced vertically to the SiC–Al interface into a plate. After mechanically polishing the plate to a thickness of about 50 μm, it was further machined with an argon ion thinning machine (Edwards, Type E306) to form a thin foil for TEM observation.

The specimens were primarily examined with a 200 kV transmission electron microscope H-700 (Hitachi Co., Ltd). For high resolution observations, H-1250 (Hitachi Co., Ltd.) 1000 kV high voltage electron microscope (HVEM) was used.

A typical micorgraph of the PLS SiC–Al interface is shown in Fig. 2. A thin reaction layer of about 10 μm in thickness was detected. There were Al_4C_3 particles of about 0.1 to 1 μm in diameter in the reaction layer. The electron diffraction pattern indicated the presence of aluminium metal among the Al_4C_3 particles. Fig. 3 is a high resolution micrograph of the region near the Al–Al_4C_3 interface. The interface was observed almost edge-on, and $(1\,1\,1)_{Al}$ and $(0\,0\,0\,3)_{Al_4C_3}$ are parallel to the interface in Fig. 3.

A typical micrograph of the region near the RB SiC–Al interface is shown in Fig. 4. No reaction layer is detected in this photograph. In this specimen, aluminium and free silicon in the RB SiC formed a continuous liquid phase at high temperature, therefore aluminium penetrates into the RB SiC. At the front of the aluminium-penetrated region, some cracks were found. It is considered that the cracks were formed because of difference in thermal expansion of aluminium and those of SiC and silicon.

2.2. Reaction between SiC and aluminium (X-ray powder diffraction)

A phase of Al_4C_3 was detected at the PLS SiC–Al interface, so the reaction expressed by Equation 1 seemed to occur. Therefore, quantitative analysis by X-ray powder diffraction analysis was carried out for the specimen which was a mixture of SiC and aluminium powders and heated.

Silicon carbide powders, GC No. 2000 (average grain size is 7.9 μm) and GC No. 8000 (average grain size 0.9 μm) which were supplied from Fujimi

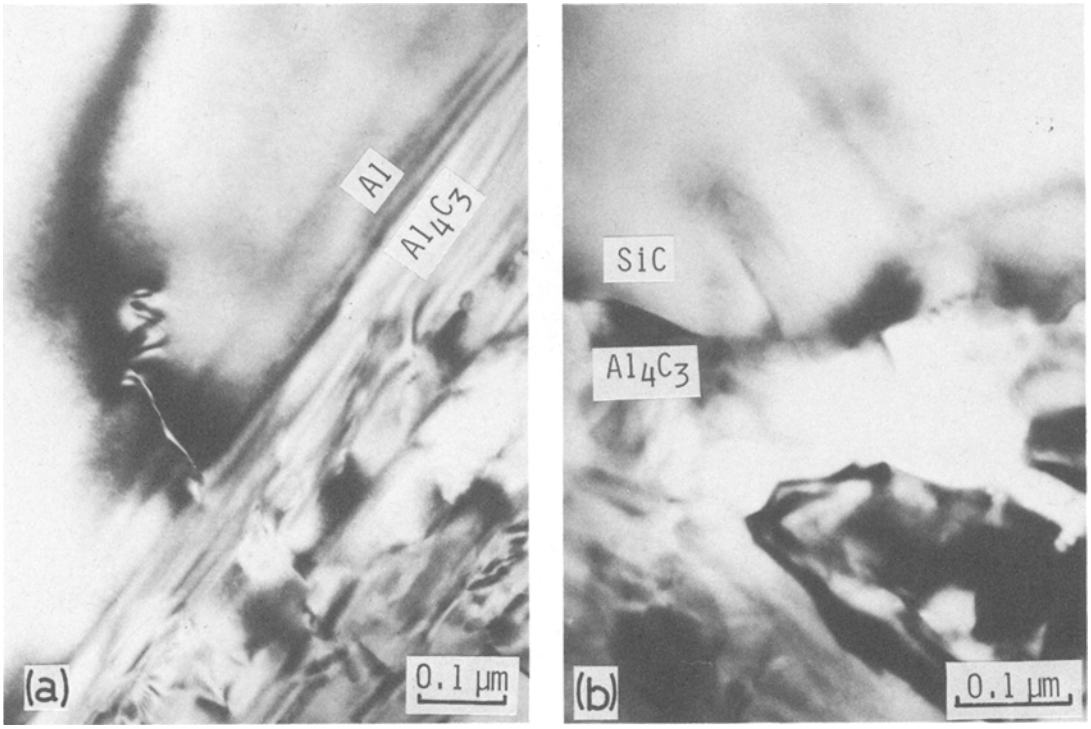

Figure 2 Transmission electron micrograph of pressureless sintered SiC–Al interface. (a) Al–Al_4C_3 and (b) Al_4C_3–SiC.

Kenmazai Kogyo Co., Ltd., Betarundum ultrafine (average grain size 0.27 µm) from Ibiden Co., Ltd., and aluminium powder (99.5 wt% purity) were used in the present investigation.

The SiC and aluminium powders were mixed in a mole ratio of 3 to 4, and pressed into a green body. Then it was heat treated in the temperature range 973 to 1473 K in a vacuum of about 10^{-2} Pa for 15 to 180 min.

In order to study the effect of free silicon on the reaction between SiC and aluminium, the same experiment was carried out by adding 1 wt% or 10 wt % silicon into aluminium powder. Silicon powder of 99.99 wt% purity was used in this experiment.

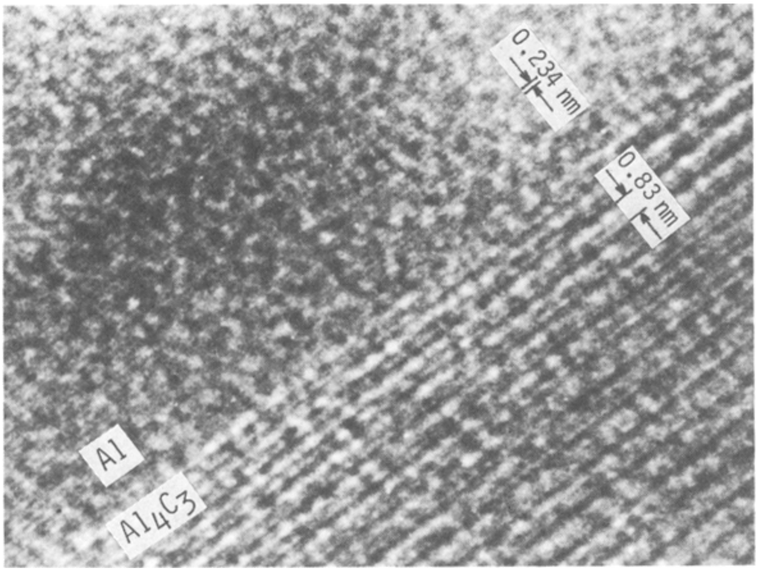

Figure 3 High voltage and high resolution transmission electron micrograph showing Al–Al_4C_3 interface. The lattice spacing of $(1\,1\,1)_{Al}$ is 0.234 nm and that of $(0\,0\,0\,3)_{Al_4C_3}$ 0.83 nm. Aluminium phase is shown in the upper left and Al_4C_3 phase lower right.

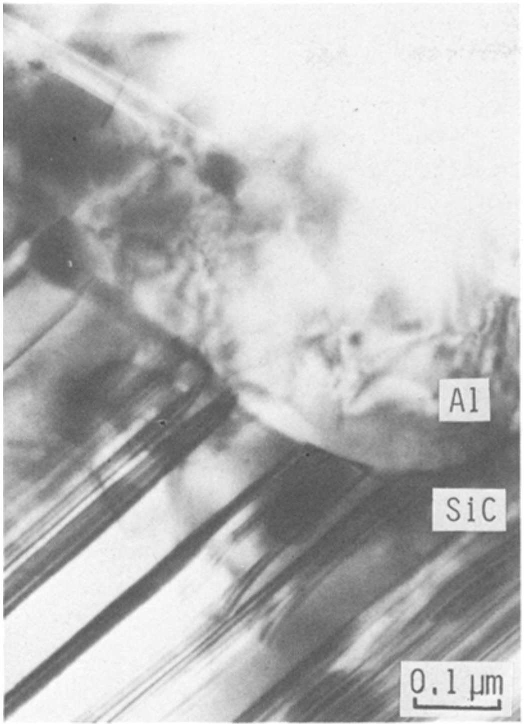

Figure 4 Transmission electron micrograph showing region near the reaction sintered SiC–Al interface.

The specimens heat treated as mentioned above were crushed into a fine powder by grinding and quantitative analysis using X-ray powder diffraction was carried out. The extent of reaction α was defined based on the amount of Al_4C_3 existed in the specimen. Namely, the materials existed as $SiC : Al : Al_4C_3 : Si = 3(1-\alpha) : 4(1-\alpha) : \alpha : 3\alpha$, where α is the extent of reaction in molar fraction. The value α was measured from changes in X-ray intensity of the diffracted peak. In this experiment, the intensity was obtained from the average of 3 to 5 peaks from each SiC, aluminium, Al_4C_3 and silicon diffraction patterns.

The results of measurement of the extent of reaction are shown in Fig. 5. Three curves in this figure are the results for the SiC specimens heat treated at 1273 K. Solid squares are that for the SiC specimen GC No. 2000 powders but heat treated at different temperatures. It seems that the reaction proceeds faster when the grain size of SiC is smaller. The extent of reaction α has saturated at a heat-treatment time of about 1 h and the saturated value of α is larger when the heat-treatment temperature is higher. It is also noted that when silicon is added into the aluminium, the extent of reaction becomes remarkably smaller.

3. Discussion

3.1. Microstructure near the SiC–Al interface

The results deduced from the TEM study are schematically shown in Fig. 6. The Al_4C_3 phase was formed at the PLS SiC–Al interface. It is considered that the origin of this difference is due to the existence of free silicon in the RB SiC. This is also confirmed in Fig. 5 which shows the reaction decreased with an increasing amount of silicon additive. In the RB SiC–Al specimen, metals of silicon which existed in the RB SiC and aluminium

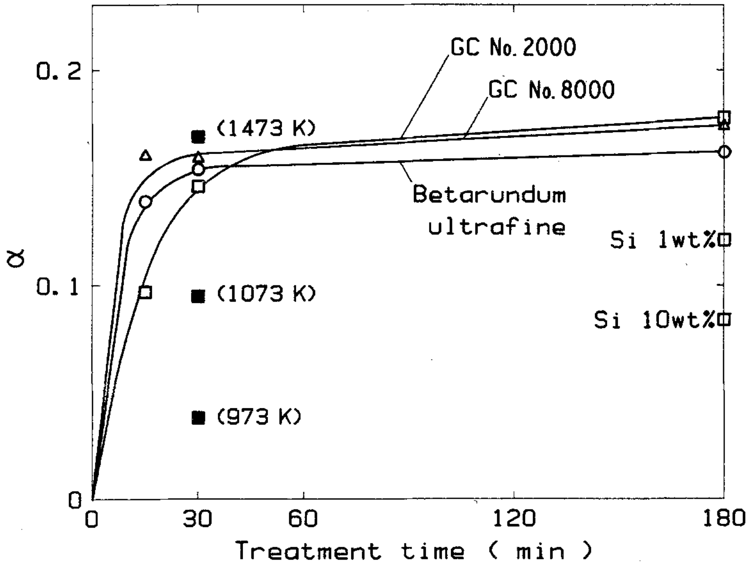

Figure 5 Extent of reaction of aluminium with SiC as a function of the heat-treatment time at 1273 K. SiC powder, □: GC No. 2000, △: GC No. 8000 and ○: Beta-rundum ultrafine. Data for siliocn addition are also shown.

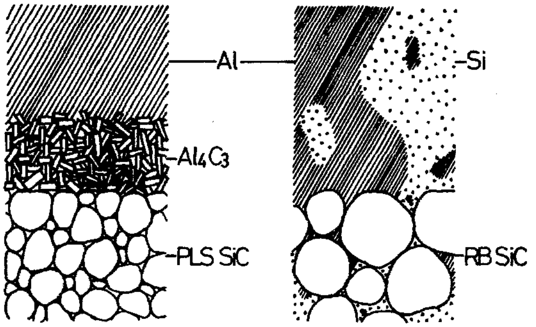

Figure 6 Schematic diagram of SiC–Al interface. PLS stands for pressureless sintered SiC and RB reaction sintered SiC.

interdiffused, and aluminium thus diffused into the RB SiC. Some cracks were found at the front of the aluminium-penetrated region. This is the reason why the bending strength of the RB SiC joints was lower at RT. In the PLS SiC joints, it is considered that the Al_4C_3 layer formed at the SiC–Al interface works effectively for yielding rigid joints.

Now, let us consider the matching between aluminium and Al_4C_3 phase at the interface shown in Fig. 3. The interplanar spacings of $(1\,1\,0)_{Al}$ and $(1\,0\,\bar{1}\,0)_{Al_4C_3}$ are close and 0.2863 and 0.2885 nm, respectively. Therefore, the difference in the interplanar spacing is only 0.8%, and good continuity between the aluminium and Al_4C_3 phase can be expected. Thus, the epitaxial relation between both phases can be expected as

$$(1\,1\,1)_{Al} \parallel (0\,0\,0\,1)_{Al_4C_3}$$

and

$$[1\,\bar{1}\,0]_{Al} \parallel [1\,0\,\bar{1}\,0]_{Al_4C_3}.$$

3.2. Thermodynamics of the reaction between SiC and aluminium

The broken line in Fig. 7 shows the calculated free energy change of the reaction expressed by Equation 1, assuming that silicon does not form a liquid phase. In this case ΔG is positive in the temperature range now considered, and the reaction does not spontaneously proceed. However, referring to the phase diagram of the Al–Si system [4], silicon dissolves into the liquid phase in the temperature range considered here. The free energy changes for this case is also shown in Fig. 7, where the calculation was made in accordance with the method of Isaikin *et al.* [5] with parameters $a_{[Si]}$, the activity of silicon in liquid aluminium. Namely,

$$\begin{aligned}\Delta G(\mathrm{J\,mol^{-1}}) = {} & 113900 - 12.06T\ln T \\ & + 8.92\times10^{-3}T^2 \\ & + 7.53\times10^{-4}T^{-1} \\ & + 21.5T + 3RT\ln a_{[Si]}\end{aligned} \qquad (2)$$

The solid lines in Fig. 7 represent that the reaction can proceed. The amount of silicon in liquid aluminium increases as the reaction proceeds, therefore $a_{[Si]}$ becomes larger and the reaction tends to saturate.

Referring to the data of Mitani and Nagai [6], the value of $a_{[Si]}$ when the reaction saturates can be converted into N_{Si}, the concentration of silicon

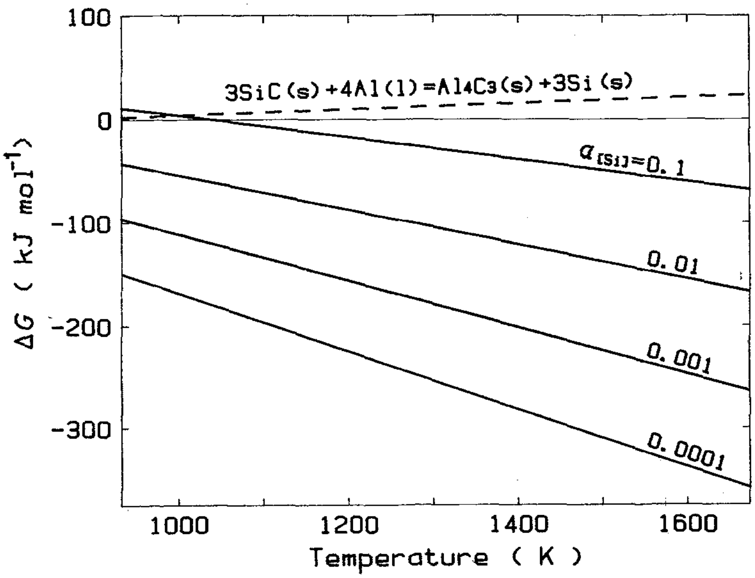

Figure 7 Free energy change of the reaction between SiC and aluminium. $a_{[Si]}$ is the activity of silicon in liquid aluminium.

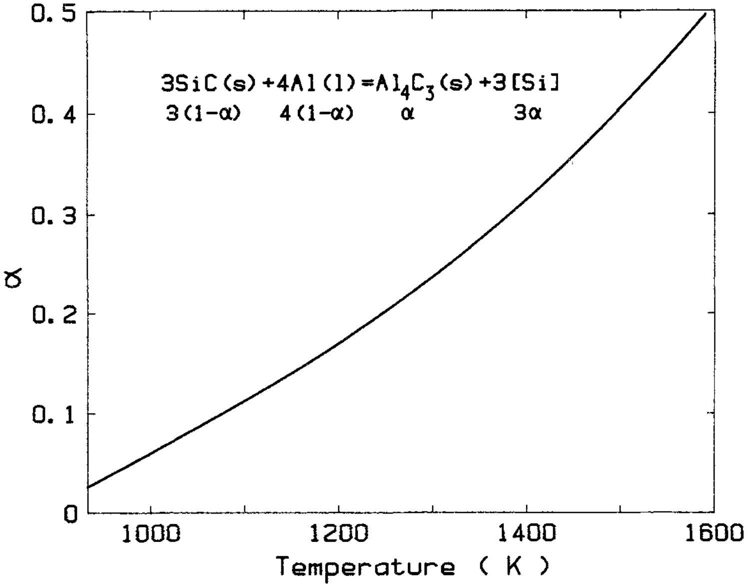

Figure 8 Relation between temperature and the saturated value of extent of reaction α.

in liquid aluminium. It is described as follows,

$$N_{\mathrm{Si}} = \frac{3\alpha}{4(1-\alpha)+3\alpha} \tag{3}$$

$$\alpha = \frac{4N_{\mathrm{Si}}}{3+N_{\mathrm{Si}}} \tag{4}$$

The relation between temperature and the saturated value α is shown in Fig. 8. It is estimated that the reaction saturates with $\alpha \simeq 0.22$ at 1273 K. When 10 wt% of silicon is added into aluminium and then heat-treated at 1273 K, the reaction will saturate with $\alpha \simeq 0.095$. Although these calculated values are slightly different from the experimental values, it is considered that they qualitatively agree with the experimental results.

It is pointed out that the compound Al_4C_3 has a tendency to be corroded by water [7]. Therefore, it is better to avoid a contact of Al_4C_3 phase with water. In order to decrease the amount of Al_4C_3 formed in the reacted region of SiC and aluminium, we should use sintered SiC which contains free silicon, add silicon into aluminium or heat treat at a low temperature for a short period of time.

4. Summary

Pressureless sintered SiC or reaction sintered SiC was heat treated in contact with aluminium at 1373 K in a vacuum of about 10^{-2} Pa for 1 h. Results of microstructural observation at the SiC–Al interface indicated that the Al_4C_3 phase was formed at the PLS SiC–Al interface, while Al_4C_3 phase was not detected at the RB SiC–Al interface. It is considered that the difference is originated from the existence of free silicon in the RB SiC. The free silicon and aluminium formed a continuous liquid phase and some cracks were found at the front of aluminium-penetrated region in RB SiC. From the results of TEM observations, the origin of change in bending strength of joints between PLS SiC and RB SiC was explained.

From the study of reaction between SiC and aluminium, it was understood that the reaction already occurred at the temperature of 933 K, the melting point of aluminium. The saturated value of the extent of reaction depended on the activity of silicon in liquid aluminium, and the reaction was decreased by the addition of silicon.

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