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Effect of a silicon sintering additive on solid state bonding of SiC to Nb

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Pressureless-sintered (PLS) SiC was joined to Nb by solid state bonding in a vacuum. The joining strength of the PLS SiC/Nb joint increases to the saturated value of 108 MPa with increasing joining pressure at a joining condition of 1673 K and 7.2 ks. This saturated value of PLS SiC/Nb joint is higher than that of the reaction sintered (RS) SiC/Nb joint. The strength of SiC itself affects the strength of the SiC/Nb joint. The high stability of the intermediate phase Nb_5Si_3 in the interface at elevated temperature leads to the high heat resistance of the joint. The thickness of the intermediate phase Nb_5Si_3 in the PLS SiC/Nb system is lower than that of the RS SiC/Nb system at a constant joining time, although the activation energy, 452 kJ mol^{-1}, of growth for the phase in the PLS SiC/Nb system is almost the same as the RS SiC/Nb system, 456 kJ mol^{-1}. The rate constant of the growth for the phase in the PLS SiC/Nb system is lower than that in the RS SiC/Nb system. The excess silicon in RS SiC promotes the formation of the Nb_5Si_3 phase at the interface between SiC and Nb.

1. Introduction

The development of joining ceramics to metals is of importance in applying ceramics. Silicon based ceramics such as SiC have attracted much interest because of their superior mechanical properties.

Joining of SiC to SiC was made using ZrO_2 [1], Ge [2] filler, Al [3] or Ti foil [4]. On the other hand, several reports of brazing SiC to metals were reported; SiC/Cu–C composite with Cu–Mn [5], SiC/SUS304 with Ag–Cu–Ti [6], SiC/Ti, Nb and Ni with Al [7] systems. Naka *et al.* [8] have indicated that the excess silicon in reaction-sintered SiC significantly reacts with Cu during brazing with Cu–Ti filler. Since they also reported the reaction of reaction-sintered SiC with Nb during solid state bonding [9], the role of the free silicon in SiC may be made clear by comparing the reaction pressureless-sintered SiC and Nb with the results of reaction-sintered SiC.

In this work, the solid state bonding of pressureless-sintered SiC with Nb without free silicon was performed in a vacuum, and the role of silicon in the joining mechanism between SiC and Nb was made clear by measuring the strength of the joint and observing the microstructures at the interface of the SiC/Nb system.

2. Experimental procedure

The pressureless-sintered SiC containing a few mass per cent of B and C, and electron-beam melted Nb in a purity of 99.9 mass% were used. SiC, 6 mm diameter and 4 mm length, was joined to Nb, 6 mm diameter and 4 mm length, in the joining conditions of 1373–1773 K, 1.8–21.6 ks and 0.49–1.96 MPa under a vacuum condition of 13.3 mPa. The joints were made by a high frequency heating graphite heater. The temperature and pressure hysteresis with a heating and cooling rate of 0.93 K s^{-1} is shown in Fig. 1. The joining strength was evaluated by fracture stress with a cross-head speed of 1.67×10^{-2} mm s^{-1}. The joining interface was investigated by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) microanalysis.

3. Results and discussion

3.1. Joining strength of the SiC/Nb joint

Fig. 2 shows the strength for the PLS SiC/Nb joint joined for 7.2 ks under 0.49 MPa as a function of joining temperature. SiC begins to join with Nb above a joining temperature of 1473 K, and raises the strength up to 53 MPa at 1773 K with increasing joining temperature. The fracture took place at the interface (○) between SiC and Nb at temperatures below 1673 K, and took place at the mixed places (●) of the interface and SiC ceramic itself at 1773 K. The fracture structure of the joint joined at 1573 K in Fig. 2 is shown in Fig. 3. The flat structures are observed at both SiC and Nb parts. As indicated later, the joint fractures between the intermediate phase in the Nb part and the SiC part.

Fig. 4 represents the change in strength of the PLS SiC/Nb joint, joined at 1673 K under 0.49 MPa with joining time. Although the change in joining time causes an increase in thickness of the intermediate phase up to a joining time of 21.6 ks, the change in

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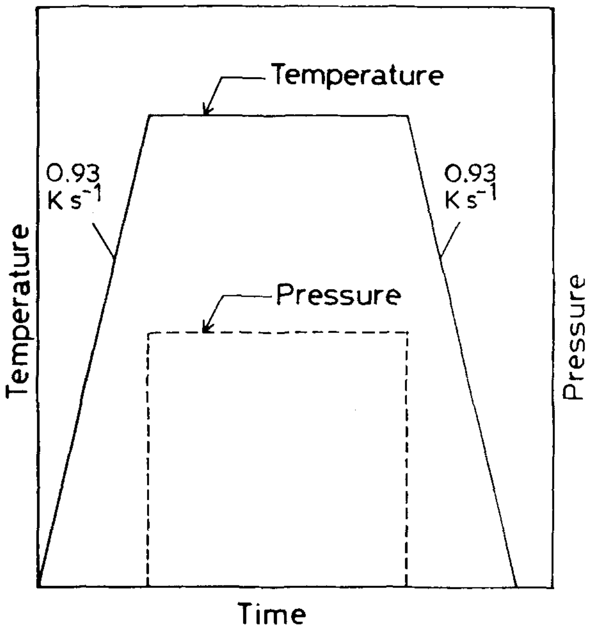


Figure 1 Temperature and pressure hysteresis during joining.

thickness of intermediate phase does not affect the structure of the interface between the PLS SiC and Nb. This leads to the small change in strength of the PLS SiC/Nb joint.

The strength of the PLS SiC/Nb joint joined at 1673 K for 7.2 ks as a function of joining pressure is shown in Fig. 5. The strength of the joint rises significantly up to 108 MPa at a joining pressure of 1.96 MPa, where the fracture surface shows the mixed structures of the interface of the joint and the SiC itself. The joining pressure effectively promotes an increase in the joining area at the interface between SiC and Nb. This gives rise to increasing the strength of the joint.

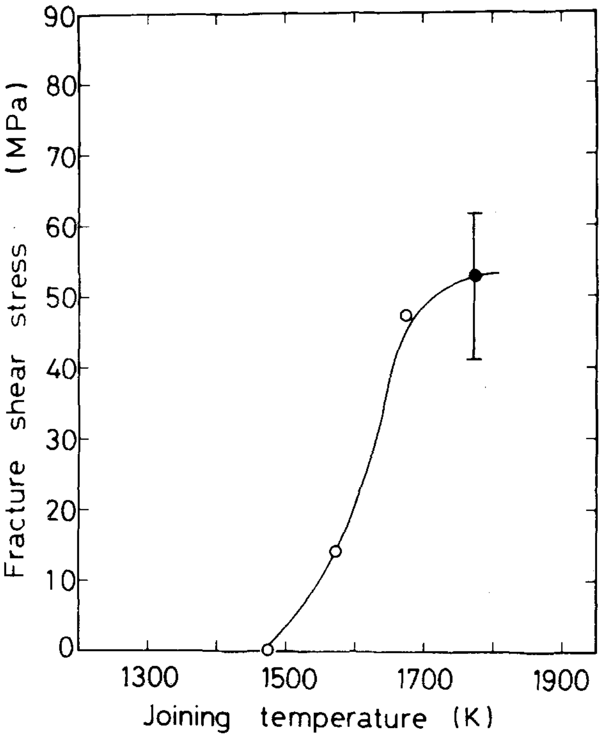


Figure 2 Change in strength of the PLS SiC/Nb joint with joining pressure (0.49 MPa) at a joining time of 7.2 ks; fractured, at (○) interface, (●) SiC and interface.

Included in the Fig. 5 are the strength of the reaction-sintered SiC (RS SiC)/Nb joint with 13 mass% free Si. The strength of the PLS SiC/Nb joint is higher than that of the RS SiC/Nb joint at higher joining pressures. The differences in joint strength result from the difference in strength of the SiC ceramics between the PLS SiC and the RS SiC, as indicated from the hardness ($H_v = 3000$ for the PLS SiC is higher than that of $H_v = 2000$ for the RS SiC).

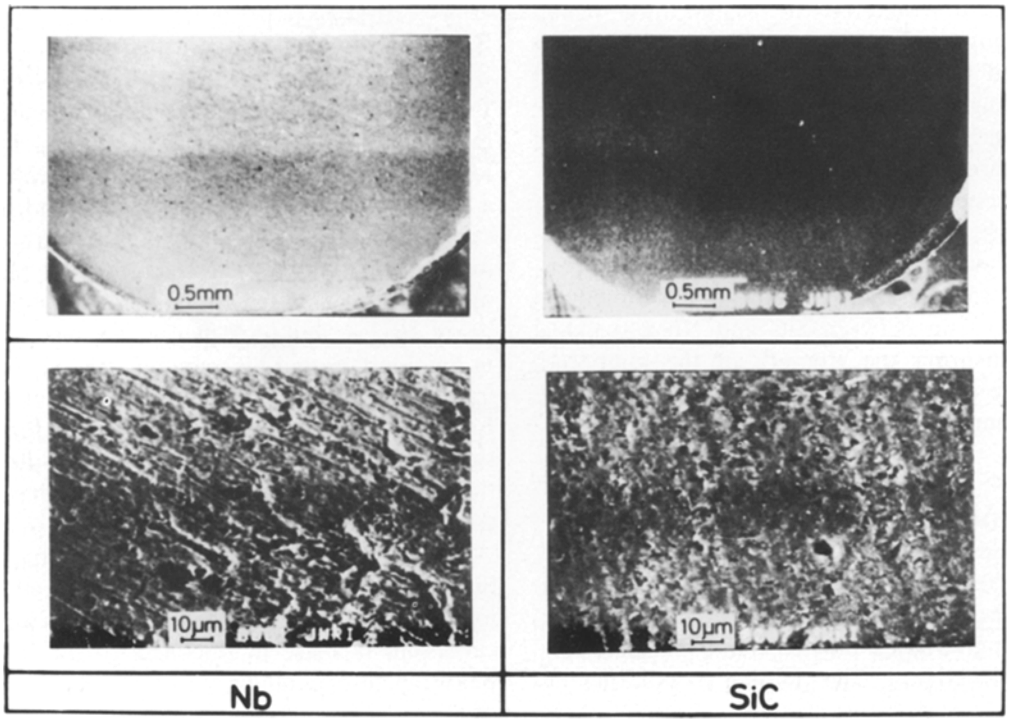


Figure 3 Fracture surface of the PLS SiC/Nb joint at room temperature, where the joint was formed at 1573 K for 7.2 ks under 0.49 MPa.

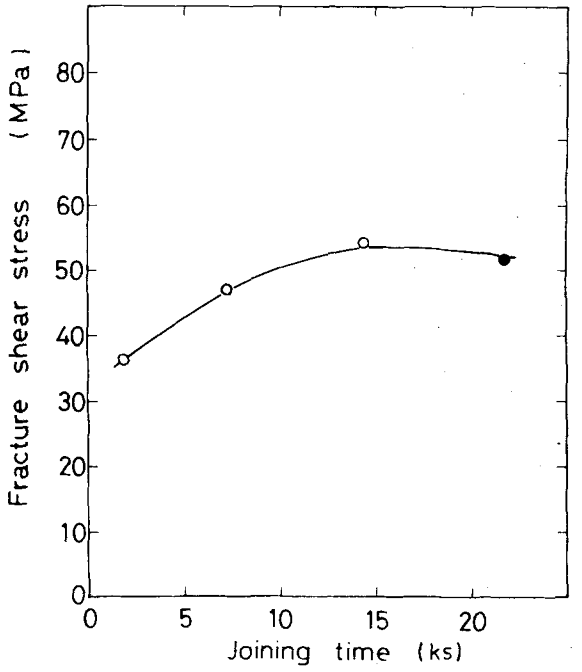


Figure 4 Change in strength of the PLS SiC/Nb joint with joining time at a joining temperature of 1673 K and under a pressure of 0.49 MPa, key as in Fig. 2.

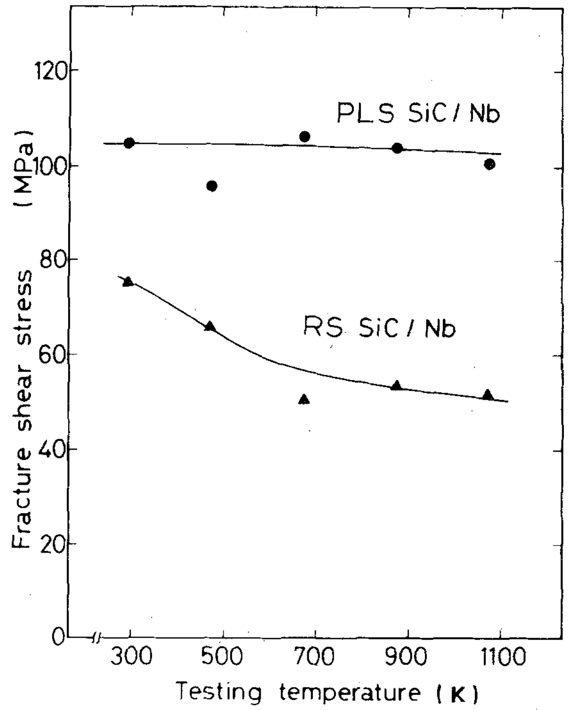


Figure 6 Change in fracture surface of the PLS SiC/Nb joint joined at 1673 K for 7.2 ks under 1.47 MPa with joining temperature.

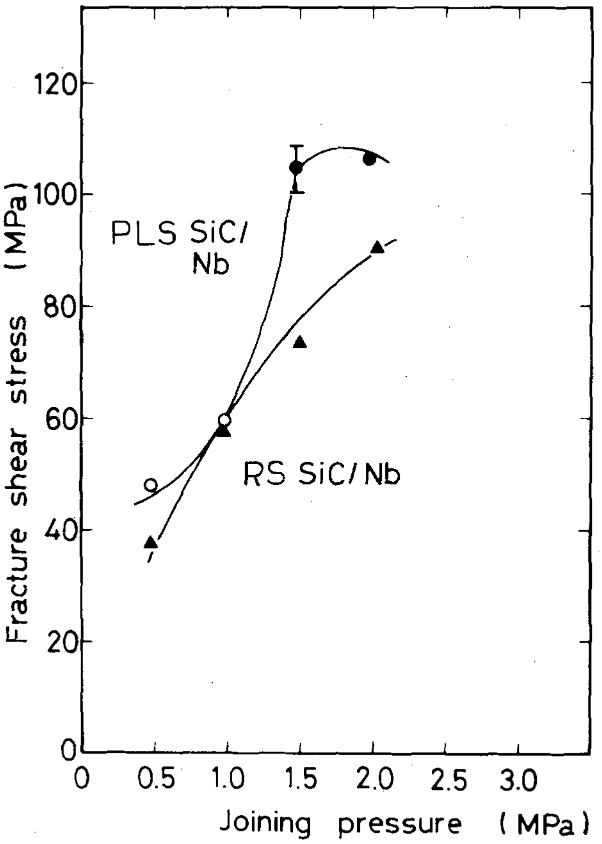


Figure 5 Change in fracture surface of the PLS SiC/Nb joint joined at 1673 K for 7.2 ks under 1.47 MPa with joining pressure, key as in Fig. 2.

The strength of the PLS SiC/Nb joint joined at 1673 K for 7.2 ks under 1.47 MPa was investigated at elevated temperatures up to 1073 K as shown in Fig. 6. The PLS SiC/Nb joint shows a little temperature dependence of strength up to 1073 K. As shown later, the intermediate phase of Nb_5Si_3 at the interface of the joint possesses high temperature stability.

The fracture structure of the PLS SiC/Nb joint tested at 1073 K in Fig. 7 also gives the high stability of the joint because the structure does not show the ductile deformed parts in the fracture surface. These results account for the small temperature dependence of strength for the PLS SiC/Nb joint.

3.2. Intermediate phase at the interface between SiC and Nb

The microstructural analyses were performed using EDX analysis and SEM. Fig. 8 shows microstructures of the interface for the joint at 1673 K under 1.47 MPa with joining time. The change in thickness of the intermediate phase is small; for example, 4.2 μm at a joining time of 21.6 ks. Fig. 9a shows the line analyses of Si and Nb and spot analysis, Fig. 9b shows the intermediate phase (i) for the PLS SiC/Nb joint at 1773 K for 21.4 ks under 0.49 MPa. The intermediate phase (i) in Fig. 9 is identified as niobium silicide (Nb_5Si_3) from EDX spot analyses and the standard specimens of niobium silicides. The X-ray diffraction measurements also gave the patterns of Nb_5Si_3. The intermediate phase in the PLS SiC/Nb joint at temperatures from 1473 K to 1773 K was Nb_5Si_3, though the intermediate phase in the RS SiC/Nb joint changed from Nb_5Si_3 to $NbSi_2$ at 1773 K [9]. The carbon in SiC during joining may be uniformly distributed in the niobium since the carbide is not observed in the PLS SiC/Nb joint.

The growth of Nb_5Si_3 is represented by Fick's law

$$x^2 = kt \qquad (1)$$

where x, t and k are the thickness of Nb_5Si_3, joining time and rate constant, respectively. Equation 1 was

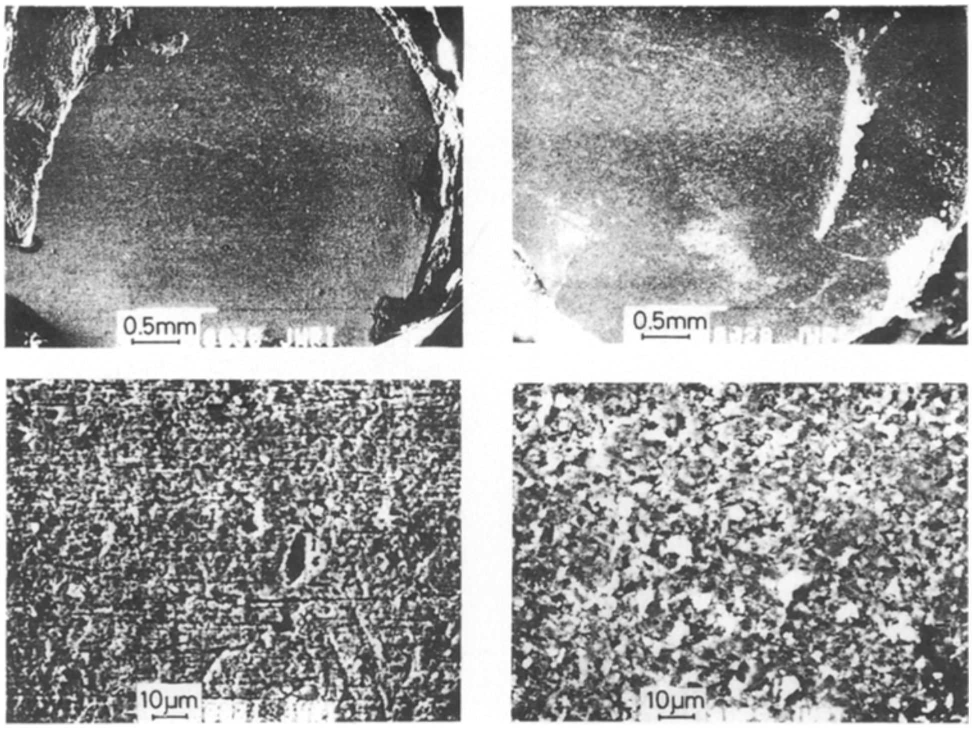
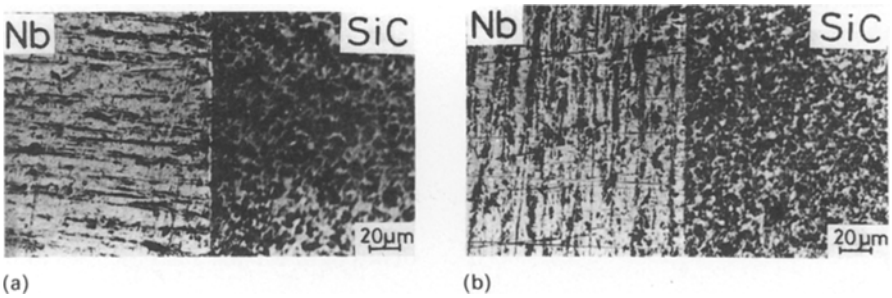


Figure 7 Fracture surface of the PLS SiC/Nb joint tested at 1073 K, where the joint was made at 1673 K for 7.2 ks under 1.47 MPa.



(a)

(b)

Figure 8 Change in microstructure of the PLS SiC/Nb joint joined at 1673 K under 1.47 MPa with joining time; (a) 1.8 ks and (b) 21.6 ks.

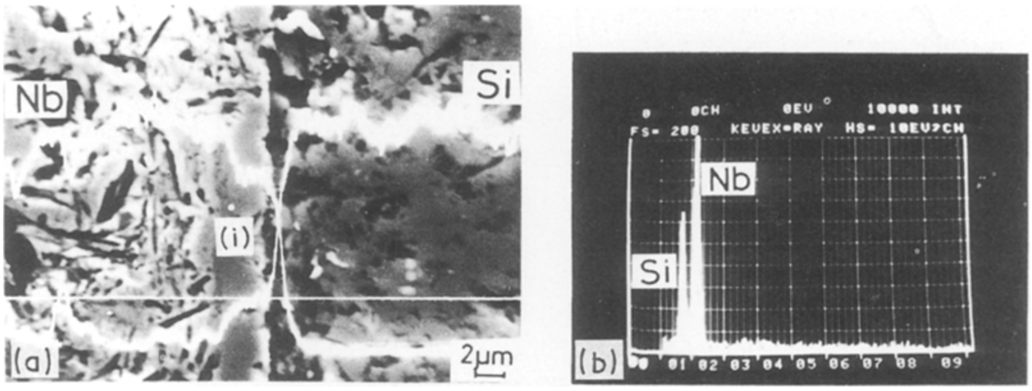


Figure 9 (a) Line analyses of Si and Nb, (b) spot analyses of the intermediate phase Nb_5Si_3 (i) in the PLS/Nb joint joined at 1773 K for 21.6 ks under 0.49 MPa.

also applied to the growth of the intermediate phase in the RS SiC/Nb joint. Further, the activation energy for the growth of Nb_5Si_3, Q, is expressed by

$$k = k_0 \exp(-Q/RT) \qquad (2)$$

From the slope at a joining time of 21.6 ks in Fig. 10, Q is estimated to be 452 kJ mol^{-1}. Included in Fig. 10 is the thickness of the intermediate phases in the RS SiC/Nb [9] and the SiC/Mo [10] at a joining time of 21.6 ks. Although this value of the PLS SiC/Nb system is lower than that of 456 kJ mol^{-1} in the RS SiC/Nb system, the thickness of intermediate phase in the PLS SiC/Nb is lower than that in the RS SiC/Nb. The sintering additive in the SiC/Nb affects the reaction between the SiC and Nb. The k_0 factor of 3.22×10^{-3} ($\text{m}^2\,\text{s}^{-1}$) for the PLS SiC/Nb system is lower

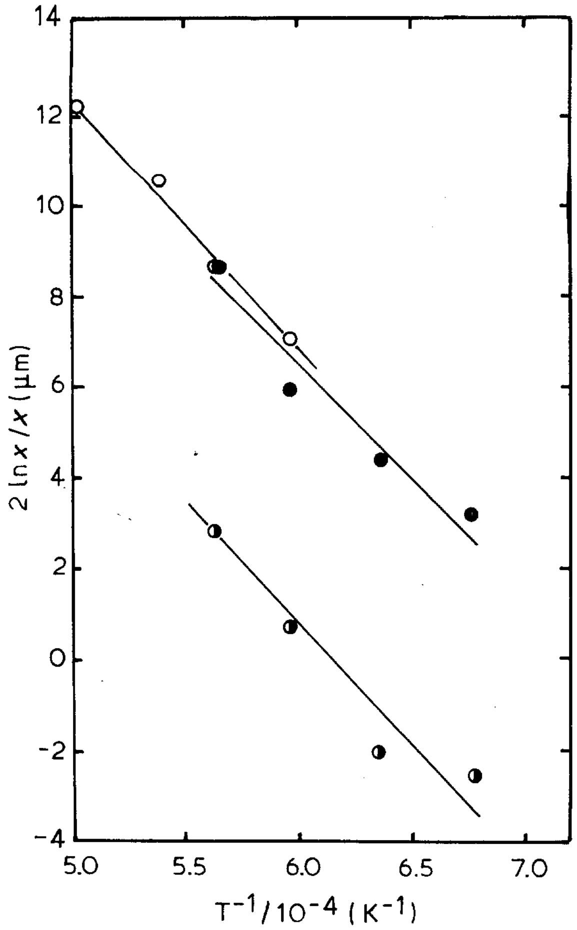


Figure 10 Comparison of thickness of the intermediate phase Nb_5Si_3 in, (◑) the PLS SiC/Nb, (●) the RS SiC/Nb and (○) the SiC/Mo systems at a joining time of 21.6 ks.

than that of 2.38 ($m^2 s^{-1}$) for the RS SiC/Nb system. The rate constant k_0 contains the frequency factor in moving atoms at the interface between the SiC and Nb. In other words, the excess silicon promotes the growth of intermediate phases, and niobium possesses more possibilities to combine with silicon at the interface between niobium and SiC in the RS SiC/Nb system.

4. Conclusion

The joining of the pressureless-sintered SiC to Nb was performed at the joining condition of 1473–1773 K, 1.8–21.6 ks and 0.49–1.96 MPa under a vacuum condition of 13.3 mPa.

The fracture strength of the PLC SiC/Nb joint increases with increasing joining time at 7.2 ks and 0.49 MPa. The joining between the SiC and Nb begins at a constant temperature, and pressure raises the strength of the joint by a small amount. The increase in joining pressure effectively raises the joining strength of the PLS SiC/Nb joint for a constant joining temperature and time; up to 108 MPa at a joining condition of 7.2 ks and 1673 K. This saturated value of the PLS SiC/Nb joint is higher than that of the RS SiC/Nb joint. The strength of the SiC itself affects the strength of the SiC/Nb joint.

The intermediate phase Nb_5Si_3 at the interface between the PLS SiC and Nb is grown by Fick's law and the activation energy for growth is 452 kJ mol^{-1}. The growth rate of Nb_5Si_3 in the PLS SiC/Nb system is much lower than that in the RS SiC/Nb system. The excess Si in the RS SiC promotes the growth of the intermediate phase.

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