Heat-Resistant Brazing of Ceramics (Report I)†

— Brazing of SiC Using Ni-Ti Filler Metals —

Masaaki NAKA*, Hiroshi TANIGUCHI and Ikuo OKAMOTO*****

Abstract

SiC was brazed to SiC using Ni-xTi filler metals (x = 0–50 at%) in a vacuum. The strength and microstructure of SiC joint were investigated by fracture shear loading and electron probe microanalysis, respectively.

The strength of SiC joint brazed at 1823 K for 1.8 ks increases with an increase in Ti content in Ni-Ti fillers. The nickel in Ni-Ti fillers with Ti content of 25 at% or below directly reacts with SiC and forms free graphite and Ni_5Si_2 silicide. The addition of 25 at% or more Ti content to Ni filler suppresses the free graphite formation and forms the TiC carbide.

SiC joint brazred with Ni-50Ti filler exhibits the superior strength at elevated temperatures up to 973 K. The dispersion hardening of TiC carbide in joinig layer is attributable to the strengthening of SiC joint.

KEY WORDS : (Ceramic Joining) (Joining) (Brazing) (Ceramics) (Silicon Crabide) (Nickel) (Nickel Titanium Alloys) (Brazing Filler Metals) (Titanium Carbide)

1. Introduction

The new ceramics have been recieved considerable interests as structural materials such as parts in automobile engine because of their superior heat-resistant properties. However, the inherent brittleness requires the joining of ceramics. Since the filler metal for joining ceramics has to possess the high wettability against ceramics, the metals include the reactive elements such as titanium. The working temperature of filler metals, which are Ag-Cu[1] and Cu base alloys[2-4], is limited up to 773 K. The more heat-resistant filler metals expand the practical application of ceramics at higher temperature.

The present work tries to join silicon carbide to silicon carbide using Ni-Ti filler metals which possess the higher melting points than that of Ag-Cu and Cu base filler metals, and clarify the joining mechanism by observing the microstructure of joining layer.

Table1 Chemical compositions of filler metals

No.	Nominal compositions (at%)		Liqidus temperature (K)
	Ni	Ti	
1	100.0	—	1726
2	93.9	6.1	1668
3	85.0	15.0	1577
4	75.0	25.0	1653
5	61.5	38.5	1391
6	50.0	50.0	1583

2. Experimental Procedure

Ceramics used is the pressureless sintered SiC with a few percent of alumina. A serise of $Ni_{1-x}Ti_x$ alloys (x = 0–50 at%) are used as filler metals in **Table 1** which includes the melting points of alloys. The alloys possess

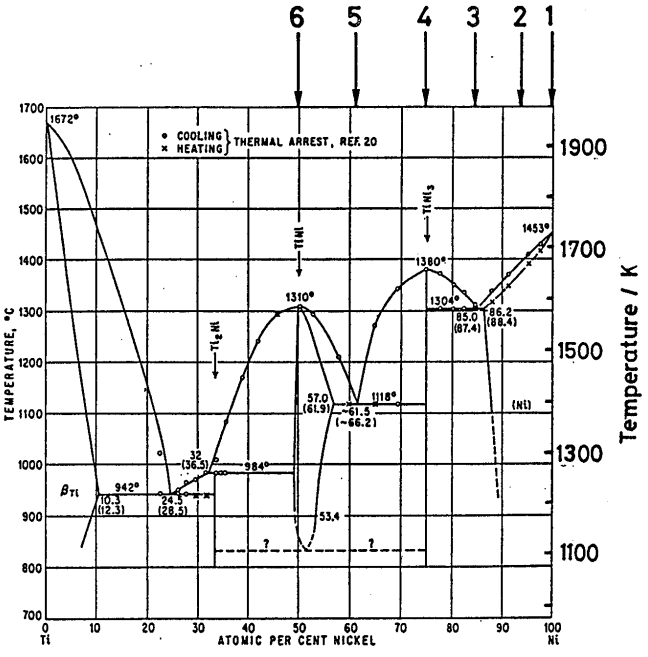

Fig. 1 Phase diagram of Ni-Ti binary alloys.

† Received on May 2, 1990

* Associate Professor

** Graduate Student (Present Address, Sumitomo Heavy Mechanical Industry Co. Ltd.)

*** Professor Emeritus

Transactions of JWRI is published by Welding Research Institute of Osaka University, Ibaraki, Osaka 567, Japan

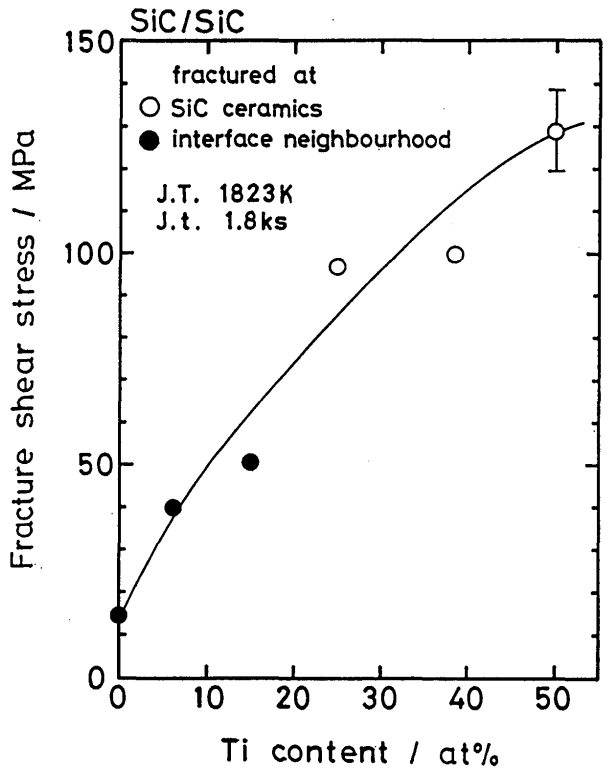

Fig. 2 Ti content dependence of strength for SiC/SiC joint with Ni-50Ti filler brazed at 1823 K for 1.8 ks.

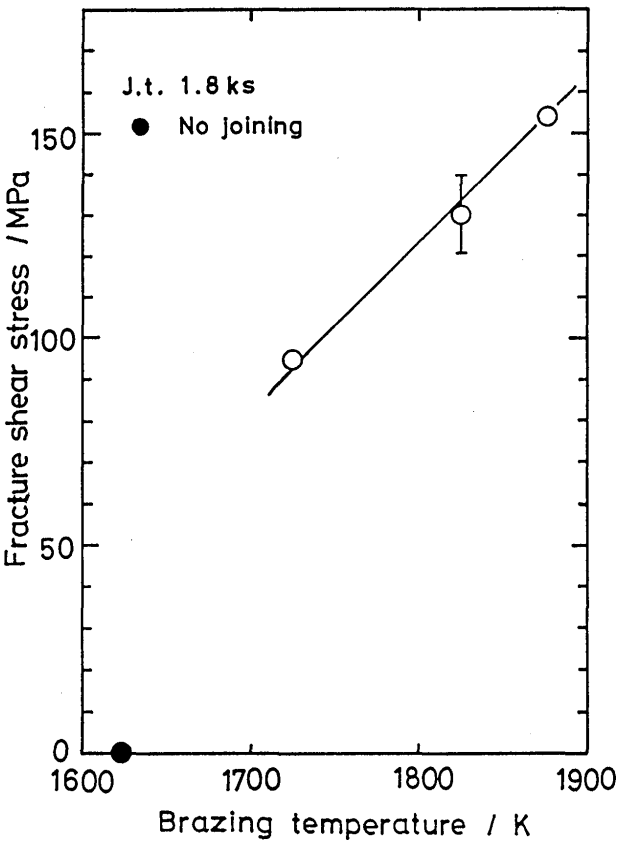

Fig. 3 Brazing temperture dependence of strength for SiC/SiC joint with Ni-50Ti filler brazed for 1.8 ks.

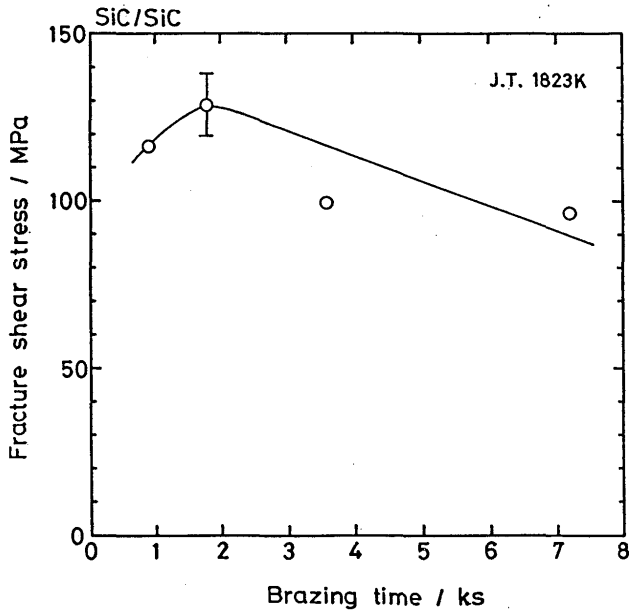

Fig. 4 Brazing time dependence of strength for SiC/SiC joint with Ni-50Ti filler brazed at 1823 K.

the melting temperatures of 1383 K or higher and the compositions of the alloys are indicated in Ni-Ti phase diagram in **Fig. 1**[5].

SiC of 6 mm diameter and 3 mm thickness and SiC of 15 mm diameter and 3 mm thickness were used for a lap joint using Ni-Ti filler metal of 6 mm in diameter and 0.1 mm in thickness.

The brazing of SiC to SiC was performed under a load of 10 g with heating and cooling rates of 0.44/s in a vacuum of 1.33 mPa. The strength of SiC/SiC joint was evaluated by a fracture loading with a cross head spead of 1.7×10^{-2} mm/s. The reaction phases in joining layer were analysed by means of EPM analyser.

3. Results and Discussion

3.1 Joining strength of SiC/SiC joint

Figure 2 shows the Ti content dependence of strength for SiC joint with Ni-Ti filler metals brazed at 1823 K for 1.8 Ks. The strength of SiC increases with increasing Ti content form 14 MPa for Ni filler to 129 MPa for Ni-50Ti filler. In the figure the soild and open markes represent the fracture positions of the interface neighborhood and SiC ceramics near the interface for SiC joints, respectively. The SiC joints with Ni-0–15 at% Ti fillers which possess the low strength fracture at the interface between SiC and alloys, and the SiC joints with 25–50 at% Ti possess the high strength fracture at SiC ceramics itself. The improvement of wettability of molten alloys and the formation of reaction phases with titanium in alloys are attributable to the increase in strength of SiC

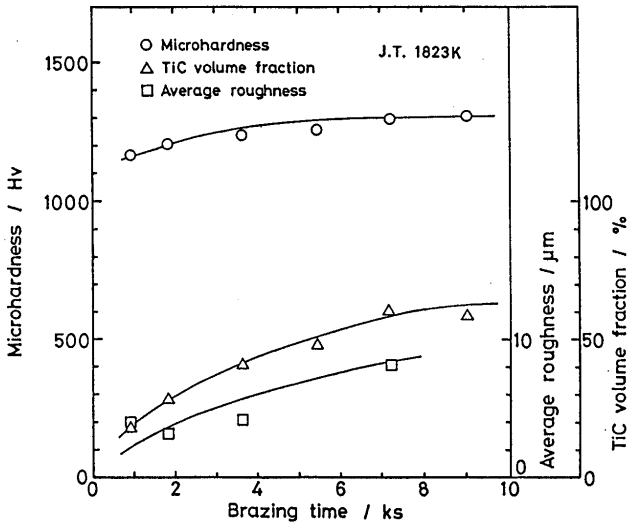

Fig. 5 Change in microhardness, TiC volume fraction and average roughness of SiC/Ni-50Ti/SiC joint with brazing time.

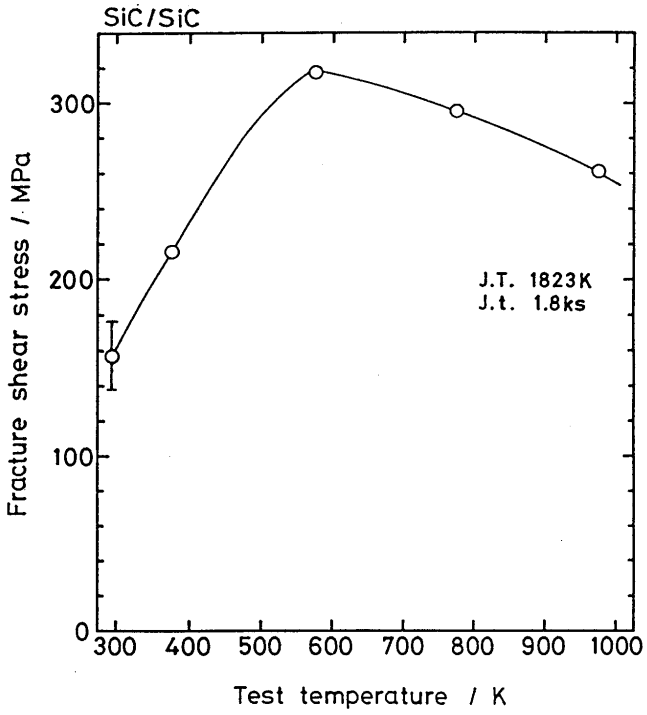

Fig. 6 Testing temperture dependence of strength for SiC/SiC joint with Ni-50Ti filler brazed at 1823 K for 1.8 ks.

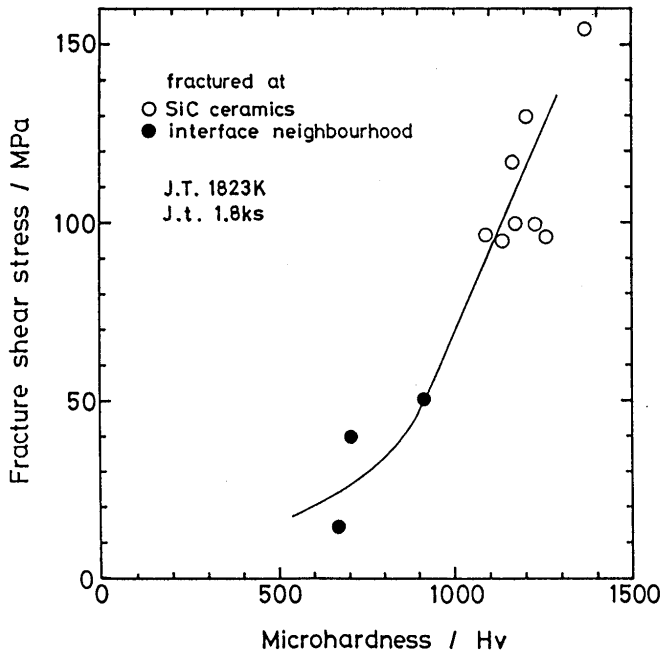

Fig. 7 Relationship between strength of SiC/Ni-Ti/SiC joint and microhardness of joinig layer.

joint as descrived later.

The change in strength of SiC joint using Ni-50Ti filler with brazing temperature is shown in **Fig. 3.** The strength of SiC joint rises with brazing temperature from 95 MPa at 1723 K to 154 MPa at 1873 K. Any SiC joint fractured at SiC itself. Ti in alloy reacts with SiC, and forms TiC carbide as shown in later. The formation of reaction phases results in the improvement of strength of joint.

The change in strength of SiC joint using Ni-50Ti filler with brazing time at 1823 K is shown in **Fig. 4.** The strength of SiC joint exhibits the maximum of 129 MPa at 1.8 ks, and lowers the value with longer brazing time. The change in volume fraction of TiC carbide in the joining layer formed during brazing is shown in **Fig. 5.** in which the change in average roughness at the interface between the joining layer and SiC with brazing time. The excess amounts of TiC carbides produced from the reaction of Ti with SiC reduce the strength of joint at the longer brazing time.

The effect of testing temperature on strength of SiC joint is shown in **Fig. 6** where the joint is brazed using Ni-50Ti filler brazed at 1823 K for 1.8 ks. The strength of joint significantly increases with incresing temperature from 129 MPa at room temperature to 316 MPa at 573 K. With further increasing temperture the strength of joint lowers to 262 MPa at 973 K. The release of stress in the joint, the mechanical properties of phases formed and the dispersion of TiC carbides cause the increase in strength of joint. This tendency of mechanical properties for joint gives the high heat-resistance of SiC joint brazed with the Ni-Ti filler.

The mechanical properties of joining layer in SiC joint affect the strength of joint as shown in **Fig. 7.** In the figure the strength of joint is plotted against the microhardness of joining layer where the hardness of joinig layer is given as a measure of mechanical properties. The lower strength of joining layer which comes from the insufficient reaction of Ni-Ti fillers offers the low strength of SiC joint. The proceeding of reaction

of Ti with SiC raises the strength of joinig layer, and also the strength of joint. The excess increase in hardness of joining layer exceeding 1200 causes the embrittlement, and leads to the scattering in strength of joint.

Figure 8 represents the fracture surface of SiC joint tested at elevated temperatures where the joint was brazed using Ni-50Ti filler at 1823 K for 1.8 ks. The joint fractured in SiC itself at room temperature, and in SiC and joining metals at testing temperatures of 573 to 973 K. The fracture surface doesn't exhibit the slip deformation at the high temperatures. This also accounts for the high heat-resitance of SiC joint brazed with Ni-Ti filler metals.

3.2 Microstructures of SiC/SiC joints

Figure 9 shows the microstructures of SiC joints using Ni-Ti filler metals at 1823 K for 1.8 ks. The non-joining area with voids are observed in the SiC joint with Ni filler, since the wettability of molten nickel is not good. The wettability of Ni alloys sgainst SiC is improved by increasing Ti content. The layer structure at the interface between SiC and joining layer includes the free graphite and TiC carbide for Ni-Ti fillers with Ti contentn of 25 at% or below.

The defects at the interface and the thickness of joining layer in joints decrease with increasing Ti content in Ni-Ti fillers.

Figure 10 demonstrates the microstructure and X-ray image analyses of Ni, Si and C in SiC joint with Ni filler metal brazed at 1823 K for 1.8 ks. The joining layer containing large amounts of Ni and Si is composed of Ni-Si silicide and free graphite. The nickel reacts with SiC and form nickel silicide and free graphite by the following reaction.

$$Ni + SiC \rightarrow Ni\text{-}Si + C \qquad (1)$$

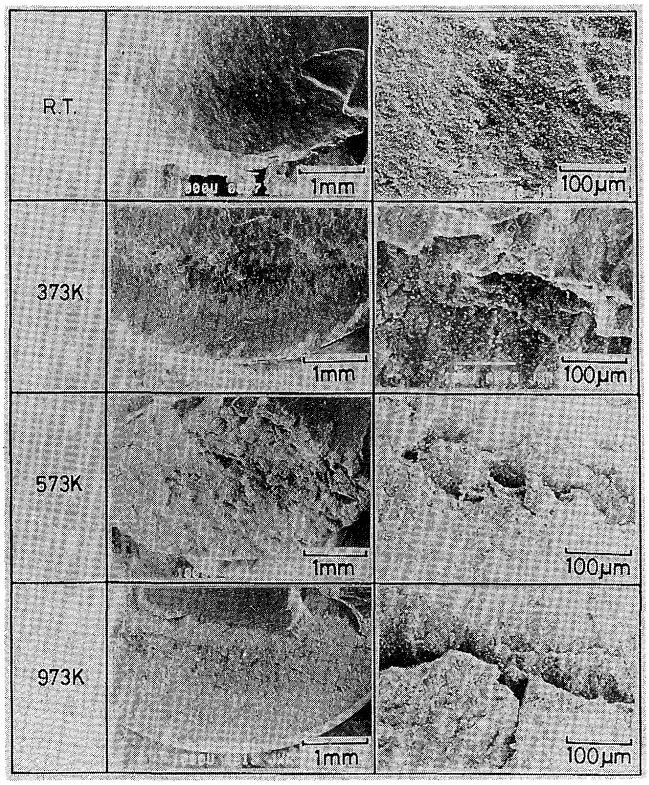

Fig. 8 Change in fractutre surface of SiC/SiC joint using Ni-50Ti filler with testing temperature.

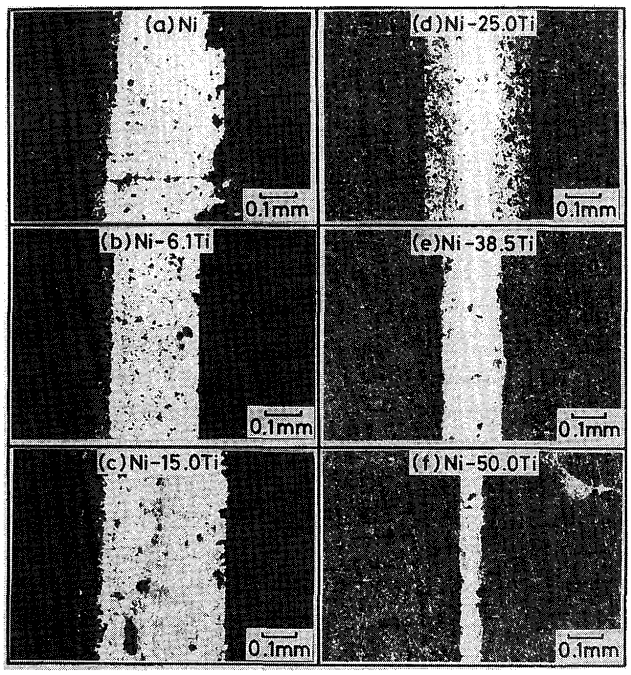

Fig. 9 Microstructure of SiC/SiC joints with Ni-Ti fillers brazed at 1823 K for 1.8 ks.

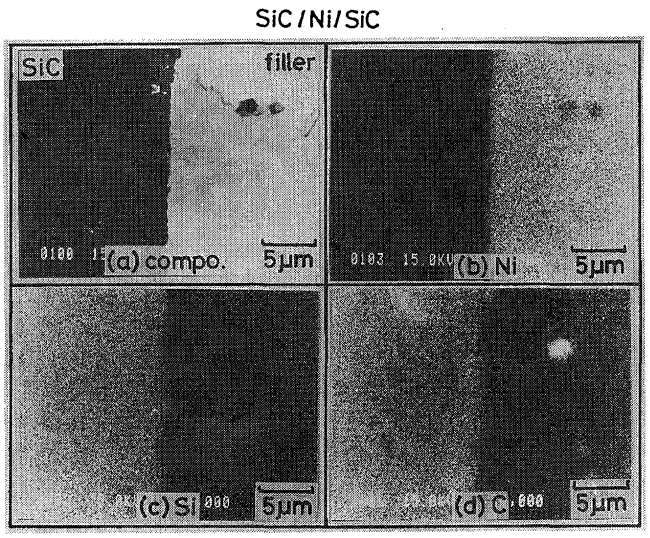

Fig. 10 Microstructure and X-ray image analyses of Ni, Si and C for SiC/Ni/SiC joint brazed at 1823 K for 1.8 ks.

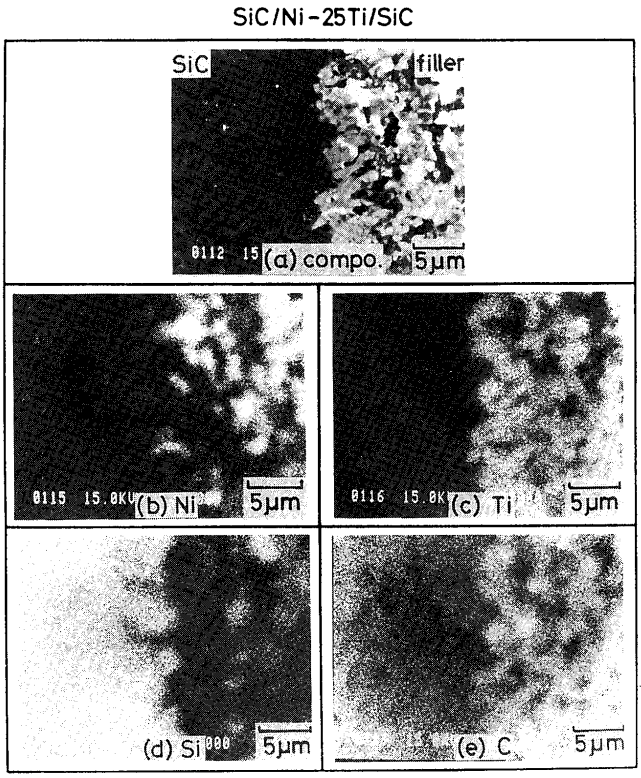

Fig. 11 Microstructure and X-ray image analyses of Ni, Ti, Si and C for SiC/Ni-25Ti/SiC joint brazed at 1823 K for 1.8 ks.

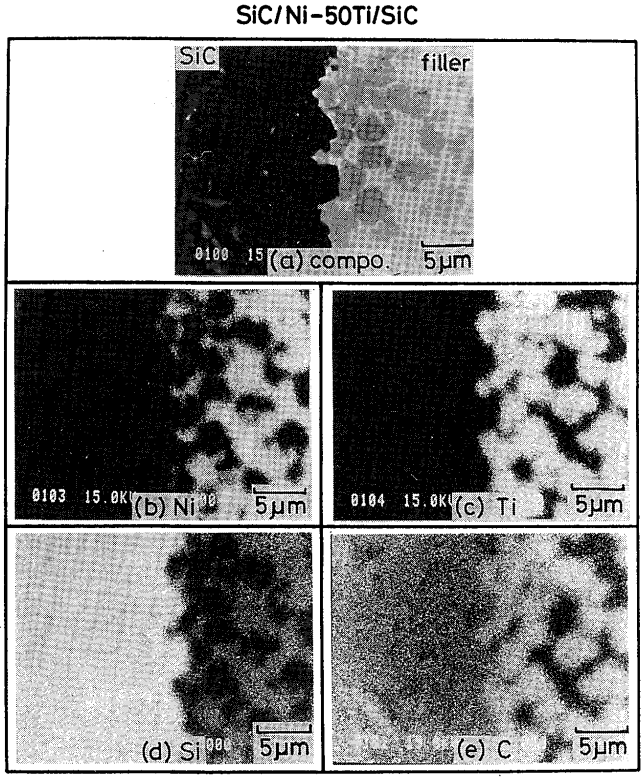

Fig. 12 Microstructure and X-ray image analyses of Ni, Ti, Si and C for SiC/Ni-50Ti/SiC joint brazed at 1823 K for 1.8 ks.

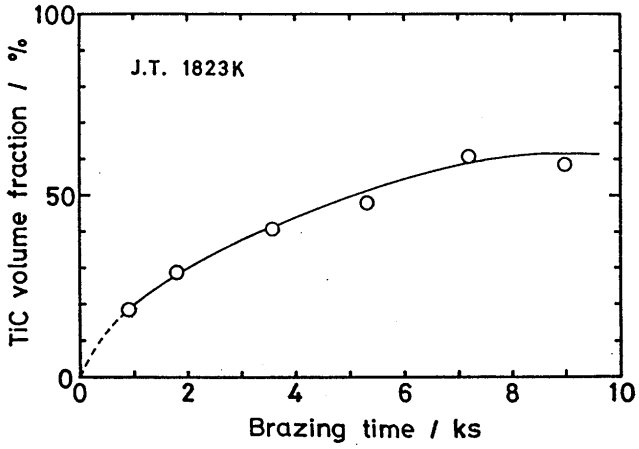

Fig. 13 Change in TiC volume fraction of SiC/Ni-50Ti/SiC joint at 1823 K with brazing time.

Table2 Quantitative analyses of TiC

(at%)

	Ti	C	Ni	Si	Al
(i)	42.85	56.60	0.50	0.05	0.00
(ii)	43.95	55.03	0.51	0.11	0.44
(iii)	42.63	56.01	1.00	0.28	0.08

The microstructure and X-ray image analyses of Ni, Si and C of SiC joint with Ni-25Ti filler brazed at 1823 K for 1.8 ks are shown in **Fig. 11.** X-ray image analyses of Ti and C elements indicate the distribution of TiC carbide in Ni-Si alloy matrix. The small amounts of graphite are observed in the joining rayer. The decrease in free graphite suggests that the formation of TiC suppresses the direct reaction of Ni with SiC.

Figure 12 shows the microstructure and X-ray image analyses of SiC joint with Ni-50Ti filler brazed at 1823 K for 1.8 ks. The granular TiC in diameter of a few μm are formed in Ni-Si alloys. The irregular interface between SiC and alloys indicates the severe reaction of Ti in alloy with SiC.

The TiC carbides are analysed by EPM analyser as shown in **Table 2.** The analyed carbon and titanium content almost correspond to the nominal content in TiC carbide. The titanium in Ni-Ti filler reacts with SiC by the following reaction.

$$Ti + SiC \rightarrow TiC + Si \quad (2)$$
$$Ni + Si \rightarrow Ni - Si \quad (3)$$

The growth rate of TiC carbide is reduced by the mutual effect of TiC carbide as shown in **Fig. 13** in which the TiC volume fraction is plotted against brazing time at 1823 K. During the growth of TiC carbide in joining

layer, the TiC carbide affects mutually the growth of other TiC carbide and further, the TiC carbide takes away the titanium in molten alloys around the other TiC carbide.

The growth of TiC carbide under the mutual effect of the carbide during brazing is expressed by Johnson-Mehl equation.

$$ln\ 1/\ (1-y) = (kt)^n \quad (4)$$

where y is the volume fraction of TiC, and k and n are constant.

$$ln\ ln\ 1/(1-y) = n\ ln\ t + n\ ln\ k \quad (5)$$

Figure 14 gives the Johnson-Mehl relationships in the growth of TiC in SiC joint with brazing time at 1823 K. The slope of present results gives $n = 1.98$ for the growth of TiC. The value of n is larger than $n = 0.5$ in the growth of metal nitride in Si_3N_4/Cu alloy joint[6]. The nucleation and growth mechanism of TiC carbide in the present system is diffrent from the layer growth of nitride in Si_3N_4/Cu alloy. This difference in growth mechanism of compounds is attributable to the difference of n in Johnson-Mehl equation.

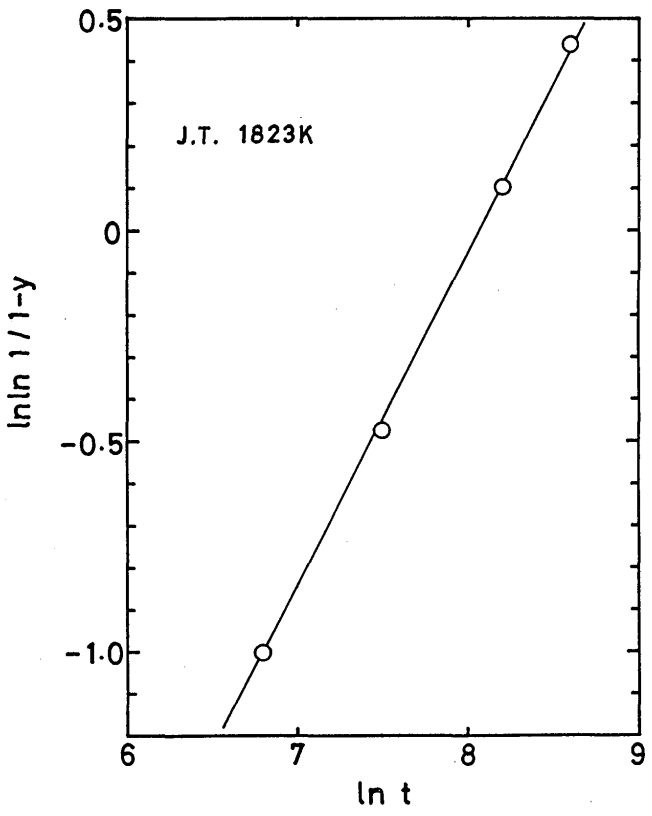

Fig. 14 ln ln 1/(1 − y) plotted with ln t, where y and t are reaction ratio and brazing time, respectively.

As shown in **Figs. 15 and 16** the alloying elements of Ni-Si alloys in joining layer are analysed for SiC joint with Ni-Ti fillers brazed at 1823 k for 1.8 ks. The average silicon content in Ni-Si alloys corresponds to 29 at% Si content in γ -Ni_5Si_2. The aluminum which is added as sintering aid to SiC is observed in Ni-Si alloys in the joining layer. Ni-Si allloys in the joining layer doesn't contain the titanium because the titanium definitely reacts with SiC. The carbon in the nickel alloys with 25 at% Ti content is analysed since the alloys include the free graphite. In the SiC with Ni alloys containing higher Ti content, the formation of TiC carbide suppress the reaction of nickel with SiC and the carbon in nickel alloys becomes lower.

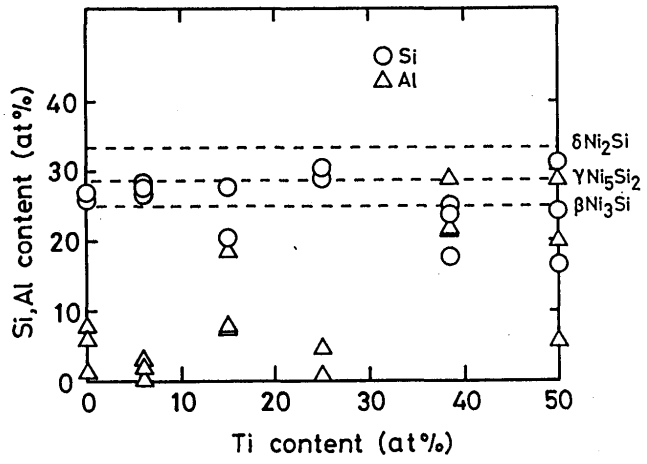

Fig. 15 Change in Si and Al content for SiC/SiC joint brazed at 1823 K for 1.8 ks with Ti content in Ni-Ti filler.

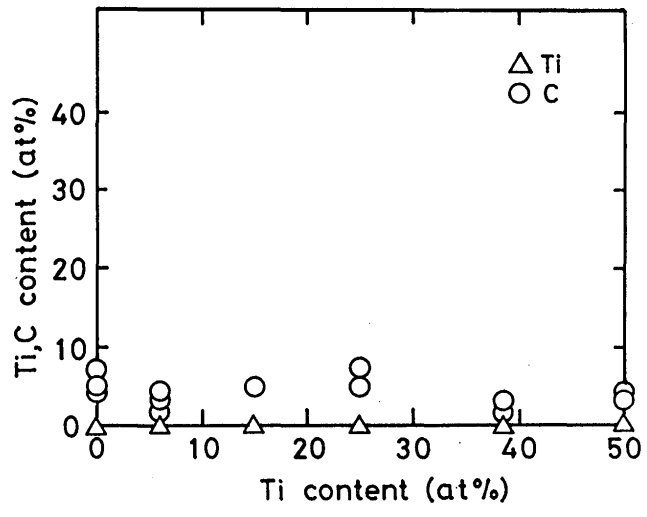

Fig. 16 Change in Ti and C content for SiC/SiC joint brazed at 1823 K for 1.8 ks with Ti content in Ni-Ti filler.

4. Conclusions

The heat-resistant brazing of SiC to SiC was performed by using Ni–xTi filler metals (x = 0–50 at%) in a vacuum. The strength and microstructure of SiC joint were examined by fracture shear loading and EPM analysis, respecvtively.

The strength of SiC joint brazed at 1823 k for 1.8 ks increases with an increase in Ti content in Ni-Ti fillers from 14 MPa for Ni filler to 129 MPa for Ni-50Ti filler. The nickel in Ni-Ti fillers with Ti content of 25 at% or below directly reacts with SiC and forms free graphite and γ-Ni_5Si_2 silicide.

The addition of 25 at% or more Ti content to Ni filler suppresses the free graphite formation and forms the TiC carbide. The improvement of mechanical property in joining layer due to the TiC dispersion results in the superior strength of SiC joint brazed with Ni-50Ti filler at high temperature.

The growth of TiC in nickel filler is expressed by Johnson-Mehl expression as $\ln 1/(1-y) = (kt)^n$, where n is 1.98. This means that the TiC carbide grows with nuclueation and growth in Ni filler.

References

1) H. Takeda: Trend in Joining Technology, Japan Weld. Soc., (1986), 32.
2) M. Naka, T. Tanaka and I. Okamoto: J. High Temp. Soc., 11 (1985), No. 6, 218.
3) M. Naka, T. Tanaka and I. Okamoto: J. High Temp. Soc., 12(1986), 81.
4) M. Naka and I. Okamoto: Materials Science and Engineering, 98(1988), 407.
5) M. Hansen: Constituion of Binary Alloys, (1958), 1051.
6) Y. Nakao: Reliability and Safty of Joining Process in Recent Composing Technology, Japan Science Committee, (1963), 10.