Phase Formation in SiC/Metal Joints at High Temperatures

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Joining of SiC to SiC was performed using Ti and Nb foils at temperatures ranging from 1373 K to 1790 K in vacuum. The change in microstructures of the SiC/Ti and SiC/Nb interfaces was investigated in detail at 1673 K and 1790 K, respectively. At a bonding time of 0.3 ks, TiC at the Ti side and a mixture of $Ti_5Si_3C_x$ +TiC at the SiC side were formed. Furthermore, a $Ti_5Si_3C_x$ layer phase appeared between SiC and mixture of $Ti_5Si_3C_x$ +TiC, upon the formation of Ti_3SiC_2 after the bonding time of 3.6 ks, the diffusion path was observed as follows: β -Ti/Ti+TiC/TiC+ $Ti_5Si_3C_x$ / $Ti_5Si_3C_x$ / Ti_3SiC_2 /SiC. At 1790 K, the diffusion path between SiC and Nb was established as Nb/Nb₂C/NbC/Nb₅Si₃C/NbC/SiC, and the NbSi₂ phase appeared at the interface between NbC adjacent to SiC and Nb₅Si₃C at the longer time of 72 ks.

Keywords: Ceramic-metal joining, interfacial structure, ceramic, metal, diffusion, SiC, Ti, Nb.

I. Introduction

An understanding of phase reactions between ceramics and metals is required in fabrication of ceramic-metal joints and ceramic reinforced metal composites. The knowledges of compounds formed and of the diffusion path between the ceramic and metal interface are necessary to control the interface structures, which essentially control the mechanical properties. SiC, which possesses superior high temperature mechanical properties, is a candidate for structural applications. The formation of Ti_5Si_3 , TiC and Ti_3SiC_2 has been reported in SiC fiber reinforced Ti composites ⁽¹⁾⁽²⁾ and SiC/Ti joints ⁽³⁾⁽⁴⁾. While these results give partial information on the reactions occurring between SiC and Ti, they do not permit to elucidate the entire sequence of phase reactions occurring at those interfaces. It is the aim of the present paper to describe in detail the interfacial phenomena, including the diffusion path, in the SiC/Ti and SiC/Nb systems, and to relate them to the Ti-Si-C and Nb-Si-C phase diagrams.

II. Experimental procedure

The materials used were cylindrical SiC rods of 6 mm diameter and 4 mm thickness, containing a few percent alumina as sintering aid, and Ti and Nb foils of 50 μ m and 12.7 μ m thickness. The bonding was done in vacuum below 1.33 mPa, using a high frequency heater equipped with a

graphite tube. The bonding temperatures changed from 1373 K to 1790 K, and bonding times from 0.3 to 144 ks under a bonding pressure of 7.26 MPa. The microstructures and phases at interfaces were investigated by x-ray diffraction (CuK α radiation) and electron probe microanalysis.

III. Results and discussion

1. Phase reactions in Ti/SiC joint

The reaction layers, which form at the SiC and Ti interface upon bonding at 1673K for times of 0.3 ks or longer, were analyzed. Figs. 1 and 2 show the evolution with time from 3.6 ks to 36 ks at 1673K of interface microstructures and of quantitative elemental compositions respectively. Initially, granular TiC phase is formed adjacent to Ti, and (TiC+ $Ti_5Si_3C_x$) duplex phase is formed adjacent to SiC. After a bonding time of 3.6 ks two additional reaction zones appeared between (TiC+ $Ti_5Si_3C_x$) and SiC: A single phase $Ti_5Si_3C_x$ zone adjacent to (TiC+ $Ti_5Si_3C_x$), and Ti_3SiC_2 zone next to SiC. $Ti_5Si_3C_x$ is a solid solution of carbon in binary Ti_5Si_3 . It has a hexagonal Nowotny-phase type crystal structure. Ti_3SiC_2 , a true ternary phase denominated T-phase, has a complex hexagonal crystal structure ⁽⁵⁾. Fig. 3 shows the x-ray diffraction patterns of interfaces revealed by successive polishing. The analysis yielded the lattice parameters of $a=0.7456$ nm, $c=0.5170$ nm for the Nowotny phase, and $a=0.3069$ nm, $c=1.767$ nm for the T-phase. These lattice parameters for the Nowotny phase are characteristic of material having a composition at the Ti rich homogeneity limit and high carbon content ($c=1$). The lattice parameter found for TiC

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Fig. 1 Microstructures of SiC/Ti/SiC.

Fig. 2 Line analyses of Ti, Si and C in SiC/Ti/SiC joints at 1673 K: (a) 3.6 ks, (b) 7.2 ks, (c) 14.4 ks, (d) 36 ks.

is $a = 0.4316\text{nm}$. For purely binary TiC such a lattice parameter corresponds to 37at% carbon [6]. However it should be noted that in the initial pattern (Fig.3A) TiC with two significantly different lattice parameters is present. One, assumed to belong to the granular TiC, is rather small ($a = 0.4286\text{nm}$) indicating very low carbon content. The other lattice parameter, assumed to belong to TiC in the duplex $\text{Ti}_5\text{Si}_3\text{C}_x + \text{TiC}$ zone, is rather large ($a = 0.4353\text{nm}$) indicating very high carbon content. Unreacted titanium is still observed at the central part of the SiC/Ti/SiC couple at this bonding time. As will be discussed below, the sequence of phases observed at these bonding conditions shows the complete diffusion path between SiC and Ti.

After longer bonding time no more unreacted Ti remains. Upon bonding for 14.4 ks the central part of the couple is a $\text{TiC} + \text{Ti}_5\text{Si}_3\text{C}_x$ zone, and the thickness of Ti_3SiC_2 layer increases significantly. Microprobe analysis shows the chemical composition for $\text{Ti}_5\text{Si}_3\text{C}_x$ and Ti_3SiC_2 to be Ti(bal.), Si(28.9-31.5at%), C(12.8-16.6at%), and Ti(bal.), Si(14.7-16.5at%), C(35.2-38.1at%) respectively. Microprobe analysis of the granular TiC yields 34.7-39.1at% carbon and about 1at% silicon. These results match very well with the XRD data.

At the bonding time of 36 ks, the additional formation of TiSi_2 in the interface zone is observed. Microstructural features, such as shape of the grains as well as growth with T-phase, indicate, that TiSi_2 has been formed from a liquid phase rather than by a solid state reaction. The evolution of the interfacial microstructures as described above is shown in Fig. 4.

Fig. 5 shows an isothermal section of the system Ti-Si-C proposed for 1673K. It is based on the assumptions, that all tie lines observed for 1373K (7) and 1473K (6) are stable at 1673K, except that the silicon rich liquid phase, which dissolves considerable amounts of carbon, coexists with Ti_3SiC_2 . The dotted line superimposed on this isothermal section indicates the diffusion path as deduced from the phase sequence observed after bonding SiC with Ti at 1673K for 3.6 ks. At these conditions local equilibrium across all interfaces is established and still neither of the end members of the diffusion couple SiC/Ti is entirely consumed. Thus, the diffusion path found from the data of the present investigation is

$\beta\text{-Ti/Ti} + \text{TiC/TiC} + \text{Ti}_5\text{Si}_3\text{C}_x/\text{Ti}_5\text{Si}_3\text{C}_x/\text{Ti}_3\text{SiC}_2/\text{SiC}$, which clarifies issues unresolved in a recent compilation of SiC/metal (7).

With the overall composition of the interface zone being close to SiC on the composition line

Fig. 3 X-ray diffraction patterns of revealed interfaces for SiC/SiC joint bonded at 1673 K for 3.6 ks.

Fig. 4 Change in microstructure of interface for SiC/Ti/SiC joint with bonding time at 1673 K.

Fig. 5 Diffusion path between Ti and SiC superimposed on proposed Ti-Si-C phase diagram at 1673 K.

connecting SiC to Ti, from Fig. 5 the occurrence of (SiC+Ti₃SiC₂+liquid) is expected at equilibrium. During cooling, the liquid phase must react with T-phase to form SiC+TiSi₂, in order to yield the (SiC+TiSi₂+T-phase) phase field observed for the Ti-Si-C system for 1473K or below ⁽⁶⁾⁽⁷⁾. Thus, the assumption of a tieline between T-phase and the liquid phase at 1673K explains the morphology of the microstructure observed at room temperature after relatively slow cooling from bonding for 36 ks at 1673K, and the microstructure of that specimen can be taken to represent the final equilibrium stage of the interfacial reaction.

The growth of compounds at an interface between dissimilar materials is often expressed as,

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

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

where x is the thickness of compounds formed, and k and k_0 are rate constants for the growth, and Q is the activation energy for growth of compound⁽⁸⁾. The rate constants for growth of compounds expressed by eq.(2) are plotted in Fig. 6. The activation energies for growth rates of

Fig. 6 Rate constants for growth of compounds in SiC/Ti system plotted with time.

Table 1 Values of Q and k_0 for reaction products of SiC/Ti system.

Composite	$Q(\text{kJ/mol})$	$k_0(\text{m}^2/\text{s})$	Refs.
Ti ₅ Si ₃ C _x +TiC	267	2.83×10^{-5}	Present work
TiC	194	2.17×10^{-8}	Present work
Ti ₅ Si ₃ C _x	242	1.07×10^{-7}	Present work
Ti ₃ SiC ₂	358	3.85×10^{-4}	Present work
SiC/Ti	250	1.84×10^{-5}	K.Kurokawa et al.
SiC/Ti	274	4.58×10^{-4}	P.Martineau et al.
SiC/Ti-6Al-4V	257	2.7×10^{-5}	P.Martineau et al.

compounds are 194, 267, 242 and 358 kJ/mol for TiC, Ti₅Si₃C_x+TiC, Ti₅Si₃C_x and Ti₃SiC₂, respectively. Since these values increase with increasing complexity of the crystallographic environment of carbon in each phase, carbon may control the growth of TiC, Ti₅Si₃C_x and Ti₃SiC₂ layers. Carbon may diffuse more easily in the phase which has a more simple crystal structure. The growth of the mixed zone of Ti₅Si₃C_x+TiC may have a different mechanism.

In table 1, the values found in the present investigation are compared with values reported in the literature of the total reaction zone growth in SiC/Ti couples ⁽¹⁾⁽⁴⁾. The kinetic constants for growth found for Ti₃SiC₂ explain why it is difficult to observe this phase at 1273 K, the experimental condition commonly used for SiC/Ti composite fabrication.

2. Phase reactions in Nb and SiC joint

Niobium of an another candidate heat-resistant metal was also bonded to SiC at 1673 K, where 12.7 μm Nb foil was used. At the initial bonding time of 1.8 ks Nb₅Si₃C_x at SiC side and Nb₂C at Nb side are formed at the interface between SiC and Nb. With the longer bonding time of 14.4 ks carbon and silicon diffuse from SiC to Nb side, and another carbide of NbC accompanying Nb₂C is formed at Nb side in the microstructure and x-ray image analyses of elements for SiC/Nb/SiC joint of Fig. 7. The thin NbC is also observed by revealing the interface between SiC and Nb₅Si₃C_x as shown in Fig. 8. The complete diffusion path between Nb and SiC is formed at this bonding time, and the path is expressed as Nb/Nb₂C/NbC/Nb₅Si₃C_x/NbC/SiC. After longer bonding time of 72 ks Nb is consumed, and the microstructure of the joint reaches to the equilibrium by appearing NbSi₂. The diffusion path is drawn on the phase diagram of Nb-Si-C. Silicon and carbon diffuse from SiC, and form NbC, Nb₅Si₃C_x, NbC and Nb₂C. In other word, the diffusion path is predicted by using the phase diagram.

Fig. 7 Microstructure and x-ray image analyses of elements in SiC/Nb/SiC joint bonded at 1790K for 14.4 ks.

Fig. 8 Microstructure and x-ray image analyses of the revealed interface between SiC and Nb₅Si₃C_x bonded at 1790 K for 36 ks.

Fig. 9 Diffusion path between Nb and SiC on Nb-Si-C phase diagram at 1790 K.

IV. Conclusions

The compounds formed at the interface between SiC and Ti were investigated at bonding temperatures from 1373 to 1773 K in vacuum. At a bonding temperature of 1673 K, TiC next to Ti and a mixture of the Ti₅Si₃C_x+TiC phases next to SiC are formed at a beginning of bonding. Ti₅Si₃C_x single phase has appeared at a bonding time of 0.9 ks. At a bonding time of 3.6 ks, the diffusion path between SiC and Ti at 1673 K could be observed as,

β -Ti/Ti+TiC/Ti₅Si₃C_x+TiC/Ti₅Si₃C_x/Ti₃SiC₂/SiC. This path is consistent with the Ti-Si-C ternary phase diagram, confirming the local equilibrium at the interfaces between the compounds formed at the SiC/Ti couples. The activation energies for growth of compounds formed at 1673 K were 194, 242, and 358 kJ/mol for TiC, Ti₅Si₃C_x and Ti₃SiC₂, respectively. The value for a mixed zone of Ti₅Si₃C_x +TiC was 267 kJ/mol. After further bonding time Ti was consumed and the structure of the interface proceeded towards the equilibrium state. A liquid phase occurred, which formed TiSi₂ upon cooling.

At 1790 K SiC was bonded to SiC using Nb foil the diffusion path was established at a bonding time of 7.2 ks or more as,

Nb/Nb₂C/NbC/Nb₅Si₃C_x/NbC/SiC.

This path was also predicted by using Nb-Si-C phase diagram. At a longer bonding time the joining structure reached to the equilibrium, and formed NbSi₂.

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