Interfacial Structure of Metal-Ceramic Joints

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On joining of metals to ceramics, chemical reaction at the bonding interfaces is unavoidable in most of the combinations of ceramics and metals including brazes except for a few special cases. Thermodynamic possibility of the chemical reaction and the resulted interfacial structure are compared with the experimental results in the cases of silicon nitride and silicon carbide ceramics. The influence of the reaction products on the bond strength of the joints and the effect of impurities on the interfacial reaction are discussed.

KEY WORDS: joining; interfacial structure; interfacial reaction; silicon nitride; silicon carbide; alumina; brazing material; reaction product; silicide; coherent interface.

1. Introduction

Joining of metals to ceramics has been widely practiced in fabricating structural components to utilize the favorable characteristics of the engineering ceramics, such as high strength, high hardness, high wear-resistance, high thermal resistance, and so forth. In order to achieve successful joining, however, there are two main problems to be overcome: one is the achievement of well bonded metal/ceramic interfaces free from unbonded areas and the other is the effective relaxation of thermal stress, which originates from the thermal expansion mismatch between metallic and ceramic parts to be joined. In this case, sheets of suitable metallic materials are inserted between the two parts to decrease the residual stress.

Bonding mechanisms are of interest in order to establish the reliable metal-ceramic joining technique. The chemical reactions and the microstructures at metal-ceramic interfaces have been investigated extensively for a number of couples of metals and ceramics, because they can relate to the bond strength and the reliability of metal-ceramic joints. This paper focuses on recent studies and reviews the interfacial structures of metal-ceramic joints and the formation of reaction products through the consideration of the reactivity of metals to structural ceramics, such as silicon nitride and silicon carbide.

2. Creation of Metal-Ceramic Interfaces

Solid-state bonding has possibility to produce a stable interfacial structure at high temperatures. A high pressure and temperature are necessary, however, for a good contact between the faying surfaces of metal and ceramic. Under these conditions the metal deforms first to make the contact of both the faying surfaces complete. Next, the metal at the interface recrystallizes to produce a coherent interface (epitaxial interface) or a chemical reaction occurs be-

tween the metal and the ceramic. In the latter case, the species of the metal and the ceramic diffuse into the other side or produce new compounds at the interface. As a result, the interface forms into a laminated structure and new interfaces are created. In addition, the diffusion removes voids at the interface, simultaneously nucleating voids at the inner region of the metal by the Kirkendall effect. If gas evolution takes place at the interface as the result of a reaction, the gas may be left as voids or pores at and near the interface, as will be described later. It may be removed by diffusion along the interface or through the metal.

When the melting point of the reaction product was lower than the bonding temperature, a liquid phase is formed at the interface, a contact with the ceramic may be achieved and the reaction may be accelerated. Such chemical reactions are observed in many successful metal-ceramic bonding. When metallic and ceramic materials are joined by the use of a metallic braze, the braze sandwiched between both the materials melts at the brazing temperature and usually reacts chemically to both the materials. In general, the liquid metals which are wettable to a ceramic are reactive to the ceramic.

The structures at metal-ceramic interfaces are classified into the following four types, as illustrated in Fig. 1:

- (1) Non-reactive and non-penetrative,
- (2) Penetrative,
- (3) Reactive, and
- (4) Diffusive.

The interfaces which belong to Type (1) are microscopically planar and are coherent (epitaxial) or incoherent. A coherent interface has been observed in some joints, such as niobium/alumina¹⁾, platinum/alumina²⁾ and platinum/cubic zirconia³⁾ systems. The interfaces which belong to Type (2) are mainly made by penetration of metal into ceramic during joining under a high pressure at high temperatures,

Fig. 1.
Four types showing metal-ceramic interfacial structures and distribution profiles of species. Between metal and ceramic.

- (a) Non-reactive and non-penetrative
- (b) Penetrative
- (c) Reactive
- (d) Diffusive

in particular, when the composite of a mixture of both powders of the metal and the ceramic is used as interlayer to decrease thermal stress coming from the thermal expansion mismatch between the metal and the ceramic. The penetrative interface is produced with ease.⁴⁾ Therefore, the interface is complicated and not planar. The majority of metal-ceramic joints reacts chemically at the interfaces, belonging to Type (3). In some couples many kinds of compounds are formed at the interface.

On joining of a copper braze to alumina ceramics, oxygen plays an important role in the formation of interfacial structure in the oxidizing atmosphere. In this case, although copper is non-reactive to alumina, copper surfaces are oxidized and the oxide reacts with alumina and silica in additives to form aluminate and silicate. A similar phenomenon appears on metallizing of alumina ceramics using the paste consisting of both powders of manganese and molybdenum in a wet hydrogen atmosphere. In this operation, manganese is oxidized by water vapor in the atmosphere and then this oxide produces aluminate and silicate. The formation of interfacial structure in these joints is closely associated with joining atmosphere. Differing a little from the above-mentioned reactions, the reaction of an aluminium braze to silicon nitride ceramics at low temperatures around 1 050 K is also helped by oxygen as an impurity in silicon nitride ceramics, as will be described later. The mechanism for the formation of interfacial structure in such joints can be termed as variant of Type (3).

When compounds are formed as the result of the chemical reaction at the metal-ceramic interface, the coherency of the interfaces between the compound and the metal and between the compound and the ceramic has not been investigated except a few couples from the viewpoint of interfacial energy or crystallography, though it is very important, because it is related to the bond strength of the joint.

3. Reactions of Metals and Ceramics

3.1. Reactivity of Metals and Ceramics

The interfacial structure in a metal-ceramic joint relates closely to the reactivity between the metal and the ceramic which are in direct contact with each other. In order to obtain knowledge of the reactivity, it is very important to respect the changes of the standard free energy for the formation of nitrides, carbides and oxides against temperature. From these thermodynamic data, when metal was placed in contact with nitride, carbide, or oxide ceramics, we are able to predict whether the metal can decompose the ceramics to form its nitride, carbide, or oxide.

The stability of nitrides at 1 200 K decreases in the following order: nitrides of Hf, Zr, Ti, Al, Ce, Bc, Ta, Nb, V, Mg, Ca, Si, Li, Cr, In, Mn, Mo and Fe, respectively. The stability of carbides at 1 200 K decreases in the following order: carbides of Hf, Ta, Zr, Nb, Ti, V, Cr, Be, Ce, Si, W, Al, Mo, Ca, Mn and Fe, respectively. It is known that the stability of oxides at 1 200 K decreases in the following order: oxides of Y, Ca, Be, Sr, Mg, Hf, Li, Zr, Al, Ti, Ce, Si, V, Nb, Mn, Cr, Na, Ga, Mo, Fe, W, In, Ge, Sn, Co, Ni, Cd, Ta and Cu, respectively. This order shows that the stability of oxides depends on temperature, for example, the stability of alumina becomes lower than that of titanium monoxide (TiO) above 1 350 K. In other words, it is expected that alumina reacts to titanium to form titanium monoxide above 1 350 K.

Differing from the above mentioned reactions, intermetallic compounds are produced, in many cases, instead of nitrides, carbides and oxides as reaction products. In such cases, the intermetallic compounds are more stable than the nitrides carbides and oxides.

3.2. Reaction of Metals and Silicon Nitride

The chemical reaction occurring between silicon nitride and metal (M) follows one of the following three formulas:

Fig. 2. Standard free energy change per half mole of Si_3N_4 for Reaction (2) against temperature.

In Fig. 2, the change (ΔG_2°) in the free energy for Reaction (2) is plotted against temperature.⁵⁾ When the bonding temperature is above the minimum temperature as is required for Reaction (2), where the value of ΔG_2° becomes zero, Reaction (2) proceeds and forms an intermetallic compound at the interface. The free nitrogen produced by this reaction diffuses in the metal when the metal has a large solubility for nitrogen and then is removed out of this joint or remains as voids at or near the interface. The solubilities of metals at 1200 K are nil for Co, Mo, Ni and W, 1.5 at% for Nb, 5 at% for Fe, 6.5–7 at% for Cr, Ta and V, and larger for Mn, Ti and Zr. The minimum temperature for Reaction (2) is raised in the order of Zr, Nb, Ti, V, Ca, Ta, Cr, Ni, Mo, Mn, Co, Fe and W. If Reaction (2) occurs, the silicide grows and prevents direct contact between the metal and the ceramic. This decreases the amount of the metal to be supplied to the ceramic side and results in the formation of another silicide with higher silicon content.

On the other hand, the change (ΔG_3°) in the free energy for Reaction (3) can be calculated from the changes of the standard free energy for the formation of nitrides. The value of ΔG_3° for many systems is almost independent of temperature.

(a) Zr, Ti, Nb and V cause Reaction (1) above the minimum temperature of Reaction (2).

(b) These metals cause Reaction (3) below the minimum temperature.

(c) Metals of Ni, Cr, Mo, Co, Fe and W cause only Reaction (2) above the minimum temperature

for Reaction (2). In this case, we must take notice of the formation of voids.

3.3. Reaction of Metals to Silicon Carbide

When silicon carbide is in contact with metal, Reaction follows one of the following three formulas.

The following comments may be made:

(a) Most of the metals making the reaction (2) take place, Nb, Zr, Ti, V, Ca, Cr, Ta, Mo and W, promote Reaction (5) over the whole temperature range, because the change in the free energy for Reaction (5) is almost independent of temperature except only W, and the severity of the reaction of metals to silicon carbide is lowered in the order written above.

(b) Reaction (6) is caused by Ta, Zr, Nb, Ti, V and Cr, as shown from the changes of the standard free energy for the formation of carbides.

(c) Common metals such as Nb, Zr, Ti, V, Cr and Ta are with Reaction (4) besides Reactions (5) and (6).

3.4. Prediction of Reaction Products

The thermodynamic data give us information of the formation of the reaction products. Thermodynamic knowledge enables us to predict the kinds of reaction products. However, it is difficult to predict reaction products to be formed in the other ceramic systems for lack of the data of thermodynamic properties.

In Table 1, Takashio⁶⁾ lists the results obtained by many workers as to reaction products in a lot of couples of metals and ceramics. As for metal-silicon nitride and metal-silicon carbide joints, as compared the predicted reaction products with the actually observed ones shown in Table 1, there exist some discrepancies about carbide and nitride in Al/SiC, Mo/SiC and Ti/Si₃N₄ joints. According to the prediction, Al₄C₃ and Mo₂C are not formed, while TiN is formed. The formation of Al₄C₃ in an Al/SiC joint cannot be understood from the viewpoint of thermodynamic stability, but that of Mo₂C can be understood when the joining operation was carried out at a temperature higher than 1850 K, because the stability of Mo₂C could become higher than that of SiC at 1850 K. As for the other metal-ceramic couples which are not listed in Table 1, as compared the prediction basing on thermodynamic data with experimental results, silicon carbide of practical use seems to be somewhat less stable than that used for measuring the thermodynamic properties. On the other hand, the formation of TiN is recognized in recent studies.

Table 1. Reaction products found in various metal-ceramic joints (after Takashio⁶⁾).

Ceramic	Metal	Reaction product
Al ₂ O ₃	Ti	TiO, TiAl ₃
Al ₂ O ₃	Ti	Ti ₂ O ₃ , Ti-Al-O
Al ₂ O ₃	Ti-Ni	Ti-Al-O
Al ₂ O ₃ *	Ti-Ni	TiO ₂ , TiO, Ti ₂ O ₃ , Si, SiO _y , Si-Ti-O
Al ₂ O ₃ *	Ti-Ni-Ag	TiO ₂ , TiO, Ti ₂ O ₃ , Si, SiO _y , Si-Ti-O
Al ₂ O ₃ *	Mo	MoO, MoO _y
Al ₂ O ₃ *	Mo	Al ₂ O ₃ ·3MoO ₃
Al ₂ O ₃ *	Mo-Mn	MnO, MoO ₂ , MoO _y , MnO·Al ₂ O ₃
Al ₂ O ₃ *	Mo-Mn	MnO, aMnO·bAl ₂ O ₃ ·cSiO ₂
Al ₂ O ₃	Nb	NbO _y
Al ₂ O ₃ -CaO-MgO	Nb	NbO _y
Al ₂ O ₃ -CaO-MgO-SiO ₂	Nb	NbO _y
Al ₂ O ₃ -CaO-MgO-SiO ₂ -Na ₂ O-K ₂ O	Nb	NbO _y , Na, K
Al ₂ O ₃ -CaO-MgO	Ta	TaO _y
Al ₂ O ₃ -CaO-MgO-SiO ₂	Ta	TaO _y
Al ₂ O ₃ -CaO-MgO-SiO ₂ -Na ₂ O-K ₂ O	Ta	TaO _y , Na, K
AlN	Ta	TaN
AlN	Zr-Ni	ZrN
AlN	Ti-Ni	TiN
AlN	Hf-Ni	HfN
AlN	Nb-Ni	NbN
AlN	V-Ni	AlNi, Al ₆ V
AlN	Ta-Ni	AlNi, Ta ₂ Al, Ta ₅ Al ₃
AlN	Cr-Ni	AlNi
AlN	Mo-Ni	AlNi
AlN	W-Ni	AlNi
SiC	Al	Al ₄ C ₃
SiC	Mo	Mo ₂ C, Mo ₃ Si ₂
SiC	Ti	Ti ₃ Si ₃ , TiC
SiC**	Ge	Si-Ge
Si ₃ N ₄	Ti	Ti ₃ Si ₃ , TiSi ₂
Si ₃ N ₄	Mo	Mo ₃ Si, MoSi ₂
Si ₃ N ₄	W	W ₃ Si ₂ , WSi ₂
Si ₃ N ₄	Ta	TaN, Ta ₂ Si
TiC	Ti	Ti ₂ C, TiC _y
TiC	Mo	Mo ₂ C
BN	Mo	Mo ₂ B, MoB
BN	W	W ₃ B, WB, W ₂ B ₅ , WB ₄
BN	Ta	TaN, Ta ₂ B, TaB
VC	Ti	V ₂ C, TiC

* means to contain SiO₂.

** means to contain free Si.

4. Interfacial Structure of Metal-Ceramic Joints

4.1. Reaction Products Observed at Interfaces

As mentioned in the preceding section, the reaction products created in many metal-ceramic couples can be predicted thermodynamically. However, the pre-

Fig. 3. Microstructures showing reaction products at the interfaces of titanium-alumina joints.

diction is not possible for all couples because of lack of thermodynamic properties and impurities present in the ceramics. In addition to this, when an alloy or an alloy braze is used instead of pure metal, the kinds and amount of the reaction products largely differ with those in the case of pure metal, though the reaction between the constituent elements of the alloy and the ceramic is, in general, suppressed by dilution. In contrast to this, Kurokawa and Nagasaki⁷⁾ find an interesting phenomenon on the reactivity of Ni-Cr alloy to silicon nitride ceramics; the reactivity becomes the severest with the alloy of 7 % Cr content as compared with pure nickel and the alloys of high chromium content. From their results, it is necessary to investigate the reaction products which were actually formed in metal-ceramic joints. The results obtained by many workers do not agree well to each other.

For example, Fig. 3 shows the microstructures of reaction layers produced in titanium-alumina joints which were held at 1 173, 1 273 and 1 473 K for 9 h.⁸⁾ The reaction layers consist of Ti₃Al (or Ti₂Al) when operated at 1 173 K and additionally TiAl adjacent to alumina above 1 273 K. The phases observed by Tressler *et al.*⁹⁾ are somewhat similar to the above results and consisted of a TiO phase including (Ti, Al)₂O₃, a Ti₃Al phase and a diffusion zone in this order from the alumina side when treated at 1 254 K for 940 h. These reaction products considerably differ from those in Ti/Al₂O₃ couples listed in Table 1.

Hence, on the basis of the data obtained in recent studies, the kinds and thickness of reaction products are listed for the couples of some pure metals and

Table 2. Reaction products found in metal-silicon nitride ceramics joints.

Metal (wt%)	Bonding condition				Interfacial structure Ceramic → Metal	Ref. No.
	Temp. (K)	Time (h)	Press (MPa)	Atmo- sphere		
Fe	1 473	0.5	100	V	[Fe (Si)] ₂₀	10)
Ni	1 473	0.5	100	V	[Ni ₅ Si ₃ +Ni ₂ Si] ₁ , [Ni (Si)] ₁₅	10)
Ti	1 473	0.5	100	V	[TiN] ₁ , [Ti ₅ Si ₃] ₁₀	10)
Nb	1 473	0.5	100	V	[Nb ₂ N] ₁ , [Nb ₅ Si ₃] ₂₋₃	10)
Ti	1 373	25			[TiN] ₁ , [Ti ₅ Si ₃ +Ti (Si, N)] ₂₂	11)
Mo	1 823	9		V	[MoSi ₂], [Mo ₃ Si ₂] ₂₀ , [Mo ₃ Si] ₁₀	12)
Ni-19.2Cr-5.0Al	1 423	100		V	[CrN+silicide] ₅₀ , [Ni ₂ Si+AlN] ₅₀ , [AlN] ₅₀ , [Ni ₂ Si]	13)
Fe-15Cr	1 373	1 125		Xe	[Cr (Ni, Fe) SiN] ₃₅ , [Al, Y-nitride] ₂₅	14)
Ni	1 273	121		Ar	[Ni (Si)] ₅	7)
Ni-7Cr	1 273	121		Ar	[Ni (Si, Cr)] ₃₂	7)
Ni-15Cr	1 273	121		Ar	[Ni (Si, Cr)] ₁₃	7)
Ni	1 273	1	9.8	V	[Ni (Si)] ₂	15)
20 μm Ti+Ni	1 423	1		Ar	[TiN] ₁ , [silicide] ₄₀	16)
Cu-9.13Ni-1.28Al-0.94V	1 423	0.25		Ar	[VN+V ₂ N+V ₃ Ni ₂ Si] ₁₇	17)
Cr	1 273	15			[Cr ₂ N+CrN] ₁ , [Cr ₂ Si] ₂₀	18)
Cu-Ag-2.2Ti	1 073-1 153			V	[TiN+Ti ₅ Si ₃ +TiSi ₂] ₂₋₃	19)

V: Vacuum

Table 3. Reaction products found in metal-silicon carbide ceramics joints.

Metal (wt%)	Bonding condition			Interfacial structure Ceramic → Metal	Ref. No.
	Temp. (K)	Time (h)	Atmo- sphere		
Mo	1 873	9	V	[Mo ₃ Si ₂] ₅₀ , [Mo ₃ Si ₂ +Mo ₂ C] ₁₀₀ , [Mo ₂ C] ₇₀	20)
Cr	1 373	25		[Cr ₃ Si] ₁₀ , [Cr ₂₃ C ₆ /Cr ₇ C ₃] ₁₀	21)
Ti	1 373	16		[Ti ₅ Si ₃ +TiC] ₂₀	21)
Ni	1 373	25		[Ni ₃ Si ₂ +Ni ₂ Si+Gr] ₁₂₀₀	21)
Fe	1 373	25		[Fe ₃ Si+Gr] ₁₄₀₀	21)
Ni	1 273	100		[Ni ₂ Si+Gr] ₁₃₀	23)
Al	1 373	1	V	[Al ₄ C ₃]	24)
Al	1 373	1	V	*No reaction layer	24)
Ni-19.2Cr-5.0Al	1 423	100	V	[Ni ₂ Si+Gr] ₃₀₀ , [Cr ₃ Ni ₂ SiC] ₁₀₀ , [NiAl+Cr+Ni ₂ (SiAl)] ₁₀₀ , [Ni (Si)] ₁₇₀	23)
Ni-10Cr	1 373	25	V	[Ni ₂ Si+Gr] ₁₂ , [Cr ₃ C ₂ +Cr ₇ Ni ₂ SiC+Ni ₂ Si] ₂ , [Ni ₅ Si ₂] ₂₅	22)
Ni-10Mo	1 373	25		[Ni ₂ Si+Gr] ₁₂ , [Gr] ₂₅ , [Ni ₅ Si ₂] ₃₅ , [Ni (Si)+Mo-silicide] ₂₀	22)
Ni-18.6Cr-18.1Si	1 443	0.08	V	*[Si (Ni)] ₁₅ , [Ni ₃ Si ₂ +Ni (Si)] ₁₅ , [Cr ₇ C ₃ in braze]	25)
Cr	1 273	100	V	[Cr _{5-x} Si _{3-x} C _{x+z} +SiC] ₃ , [Cr ₃ Si ₃] ₄ , [Cr ₇ C ₃ +Cr ₃ C ₂] ₃	26)
Mo	1 373	81		[Mo ₅ Si ₃] ₁ , [Mo ₂ C] ₁₀	21)
V	1 373	100		[V ₅ Si ₃] ₁ , [VC] ₄₀	21)

V: Vacuum * : Reaction-bonded silicon carbide Gr: Graphite

alloys to silicon nitride and silicon carbide ceramics in Tables 2 and 3, respectively. On the column of "Interfacial structure", the reaction product adjacent to the ceramic is written on the left side and the reaction product written on the right side is adjacent to the metal. The thickness of a reaction layer is written by the unit of μm as a subscript on the outside of brackets of the reaction product. A letter *t* means "thin".

Reaction (5) should not take place with nickel because of larger stability of SiC than Ni₃Si. However, nickel reacts to silicon carbide and produces a silicide, as shown from Table 3. If it is assumed that the stability of silicon carbide is a little lower, the kinds of reaction products in the couples in tables can be predicted, but it is difficult to estimate the thickness theoretically.

4.2. Growth of Reaction Products

Reaction products are generally brittle. As the layer of these products becomes thicker, the bond strength, at first, increases and reaches its maximum at a suitable thickness, and then decreases. Therefore, the reaction products are to be controlled in thickness to enhance bond strength. Fig. 4 shows the relationship between the bond strength and the thickness of the reaction layer for molybdenum-silicon carbide ceramics joints brazed by use of Cu-5%Cr alloy at 1 573 K in vacuum.²⁷⁾

Reaction products in a great part of metal-ceramic couples grow following the parabolic law. The thickness of the reaction layers shown in Fig. 3 is plotted against holding time in Fig. 5.⁸⁾ The growth of the reaction layer clearly follows the parabolic law. A few products, however, do not follow the parabolic law.

Fig. 4. A change of bond strength with reaction layer thickness for molybdenum-silicon nitride ceramic joints brazed with Cu-5%Cr alloy at 1575 K (after Nakao *et al.*²⁷⁾).

Fig. 5. Thickness of reaction layers shown in Fig. 3 with elapsing time at holding temperatures of 1173, 1273 and 1473 K.

According to Kurokawa and Nagasaki,²¹⁾ the growth rate of reaction layers in iron-silicon carbide and nickel-silicon carbide couples becomes considerably large after an elapsing time, as shown in Fig. 6. This might be attributed to the large solubilities of carbon and silicon in iron and nickel. Furthermore, there is another type which does not follow the parabolic growth law. Morozumi *et al.*²⁰⁾ found that the growth rate of Mo_2C in molybdenum-titanium carbide joints was constant in the case when the content of free carbon in titanium carbide was as small as 0.01 %.

Open marks: SiC-Ni
Closed marks: SiC-Fe

Fig. 6. Changes in thickness of reaction layers in iron-silicon carbide and nickel-silicon carbide couples with elapsing time at holding temperatures of 1373, 1273 and 1173 K (after Kurokawa and Nagasaki²¹⁾).

4.3. Gas Evolution

On joining of metals to silicon nitride, the metals which cause only Reaction (2) evolve nitrogen gas at the interface. The nitrogen solubilities of nickel, molybdenum, cobalt and tungsten are too small to occlude the nitrogen gas. As a result, voids are observed as a defect in the vicinity of the interface. In order to prevent this defect to grow, it is desirable for the metals to contain a strong nitriding element, such as zirconium, titanium, niobium and vanadium, which serves as a scavenger of nitrogen.

Titanium, which is powerful as a scavenger of nitrogen, is an indispensable element for a successful bonding, but the pure metal does not bond to silicon nitride because a very thin TiN layer is formed at the interface and prevents cohesion of both the materials.¹⁰⁾ If this element is alloyed into an inactive metal in dilution, TiN forms uniformly, distributes as particles in the vicinity of the interface and can contribute for raising the bond strength.¹⁹⁾ When such an alloy is used as a braze, titanium and other strong nitriding elements tend to concentrate at the interface.

4.4. Role of Impurities in Ceramics

Aluminium reacts to silicon nitride to form aluminium nitride under a sufficiently high nitrogen partial pressure, as pointed out by Andrews *et al.*²⁸⁾ When an aluminium braze is placed on silicon nitride ceramics at a low temperature of 1050 K in vacuum less than 10^{-3} Pa, the reaction layer formed at the

interface consists of a silica-alumina non-crystalline layer of 0.5–1 μm and a very thin β' sialon layer adjacent to the silicon nitride ceramic.²⁹⁾ In this case, oxygen coming from impurities and additives in the ceramics helps the formation of the interfacial structure and thus the bonding of both the aluminium and silicon nitride, which also indicates us that oxidizing the faying surface of silicon nitride ceramics is effective for the achievement of cohesive bonding between aluminium and silicon nitride ceramic.³⁰⁾

Additives in ceramics relate to the formation of the interfacial structures. Constituent elements of additives have a tendency to concentrate at the bonding interface. Fig. 7 shows typical distribution curves of yttrium, magnesium, aluminium and oxygen as additives in an iron-silicon nitride ceramic joint after the bonding operation at 1473 K for 0.5 h under a pressure of 100 MPa using a HIP.

In general, silicon carbide ceramics are severer in the reactivity to metals than silicon nitride ceramics. The amount of free silicon and free carbon in silicon carbide ceramics influences the reactivity largely.

4.5. Coherent Interfaces

As mentioned in Chap. 2, it has been experimentally established by means of high resolution electron microscopy and X-ray diffraction that some couples are bonded with a coherent interface. Even when a reaction product was produced at the interface, it is found that the reaction product is bonded to the ceramic with a coherent interface. For example, Morozumi³¹⁾ find out that there is a crystallographic relationship between SiC and Ti_3SiC_2 which was produced by a reaction at the interface of titanium and SiC . On the basis of a bonding experiment on niobium-alumina couples Ishida *et al.*³²⁾ describe that the ceramic which once dissolved into metal back-precipitates the niobium-alumina interface on cooling. Their studies were performed under good conditions, that

is, ceramics used were single crystal and their faying surfaces were oriented to be a low index plane. Although such conditions cannot be prepared in practical joining operation, their results should elucidate the bonding mechanism and give us the ways for the achievement of reliable joining technology.

Recently there are some studies concerning the bond energy among atoms in ceramic and the metallic atoms which were deposited on the ceramic surface in order to elucidate interfacial reaction fundamentally and at an atomic level.^{33,34)} Through these researches, various phenomena occurring at metal-ceramic interfaces will be made clear.

5. Conclusion

For the achievement of good cohesive metal-ceramic interfaces, the understanding and the knowledge of interfacial reaction are very important, because interfacial reaction decides the interfacial structure, which relates closely to the bond strength of the joint. Reaction products, in the case of the joints of metals to silicon nitride ceramics, can be predicted on the basis of thermodynamic consideration. On the other hand, the thickness of the reaction layers follows the parabolic law except a few examples. When alloys or alloy brazes are used as metals to be joined, the kinds and amount of the reaction products considerably differ from those in the case of pure metals.

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