High Resolution and Analytical Electron Microscopy Study of Si_3N_4 -Ni Bonded Interface

Manuel E. BRITO,¹⁾ Hiroyuki YOKOYAMA,²⁾ Yoshihiko HIROTSU and Yoshiharu MUTOH

Division of Mechanical Engineering, Nagaoka University of Technology, Kamitomioka, Nagaoka, Niigata-ken, 940-21 Japan. 1) Graduate School, Nagaoka University of Technology. 2) Graduate Student, Nagaoka University of Technology. Now at Toshiba Engineering, Horikawa-cho, Kawasaki-ku, Kawasaki, Kanagawa-ken, 210 Japan.

(Received on July 18, 1988; accepted in the final form on November 18, 1988)

A detailed characterization of the ceramic-metal interface was carried out for a Si_3N_4 -Ni system bonded in vacuum at 1 273 K. High resolution electron microscopy and analytical electron microscopy were used in the characterization of the interface. Reaction products such as nickel silicides were not present at the interface. It was demonstrated that Si_3N_4 reacts with Ni in accordance with the solid-state reaction mechanism proposed in this study. The final reaction product is thought to be Ni with Si and N in solid solution.

KEY WORDS: Si_3N_4 ; Ni; bonding; interface; reaction; high resolution electron microscopy; Analytical Electron Microscopy.

1. Introduction

Among the so-called "Fine Ceramics", Si_3N_4 has been considered for application in high temperature components. It has good resistance to wear, hardness and high strength at elevated temperatures. However, Si_3N_4 is a brittle material difficult to process and it is required in much of its applications to bond it to metals or alloys. As the result of thermal expansion mismatch between the ceramic and the metal, residual stresses are generated within the ceramic and metal and at the interface, inducing a significant reduction of the bonding strength. In order to relieve the stresses generated during the bonding process, the use of soft metals such as Ni, as an insert material has been proposed.¹⁾ Nevertheless, the bonding strength depends, also, on the nature of the structure developed at the ceramic-metal interface and, therefore, an exhaustive structural analysis of this interface is necessary in the development of reliable bonding technology.

Recently, in a macroscopic study of the interface

for a Si_3N_4 -Ni system bonded at 1 273 K in a high vacuum, the present authors have reported that Ni silicides are not present at the interface.²⁾ However, a small amount of reaction phases undetectable by X-ray diffraction may exist as thin interface layers. Thermodynamic data indicates that reactions of Si_3N_4 with Ni to form silicides start near 1 000 K.³⁾ In our previous report, we have shown that the morphology of Si_3N_4 -Ni interface changes from an original flat mode to an irregular one. This phenomenon is dependent on the time of bonding process. Also, an *in-situ* observation with high-temperature optical microscope showed that the interface undergoes a melt-like phase formation at 1 273 K for a holding time of 3 ks and that the melt-like region grows for a longer time of treatment.

In order to elucidate the reaction mechanism at the interface, the above experimental evidence should be correlated consistently. Based on these experimental evidence, only two possible models of reaction mechanisms can be considered. A scheme for both reaction mechanisms is presented in Fig. 1. Here,

Fig. 1. Schematic diagram showing the two possible reaction mechanism between Si_3N_4 and Ni in vacuum at 1 273 K.

the Si_3N_4 -Ni interface represents an extremely localized site of reaction, except the outer surface region of this interface in contact with vacuum. The decomposition of Si_3N_4 is the primary step for any of the proposed reaction mechanisms. As we can easily derive from Hincke and Bratley's data,⁴⁾ Si_3N_4 decomposes at temperatures above 1 160 K in vacuum:

In the reaction model I a kind of Ni-rich phase formation is enhanced by the decomposition, and subsequently a Si-rich phase forms at the interface by a reaction between the Ni-rich phase and the decomposed Si_3N_4 . This Si-rich silicide must be Ni_3Si with the melting point of 1 237 K. Because of the very low N_2 partial pressure, the melting would occur in a wider extension at the outer region of the interface in contact with vacuum. However, at the inner-bonded interface, only the reaction front melts to form a limited thin layer. Finally, it is expected that reaction layers composed of the Ni-rich silicide and the thin layer of Ni_3Si remain at the interface. It has been proposed that a melt formation at the Si_3N_4 -Ni interface helps to create a good contact at the interface.⁵⁾ The second possible reaction mechanism model II is shown schematically in the lower part of Fig. 1. Here, a simple solid-state reaction between the Si_3N_4 and Ni to produce the Ni-richest silicide, Ni_3Si , and/or a solid solution of Ni containing Si and N is considered. In the model II, the instantaneous raise to a relatively high partial pressure of N_2 is believed to play a fundamental role in the formation of Ni_3Si as a unique silicide reaction phase referring to the free energy of the silicide formation.³⁾ In this case, the melt-like morphology observed at the interface might be interpreted as a melt-like dynamic motion of the interface region due to a mass-transfer of Ni towards Si_3N_4 . Nickel has to fill the space after the decomposition of Si_3N_4 at 1 273 K in vacuum.

In order to examine which of the two possible reaction mechanisms proceed, we have combined the high resolution and analytical electron microscopy in a detailed local structural analysis of the interface.

Supplemental information by Auger electron spectroscopy and X-ray diffraction was utilized to help understanding the reaction mechanism.

2. Experimental

Rods 15 mm in diameter of pressure-less sintered Si_3N_4 containing less than 5 %wt of oxide additives were cut into 10 mm thick discs. The surfaces to be bonded were diamond polished to obtain optical-flat surfaces. By a similar process discs of Mo were also manufactured. After inserting foils of high purity Ni (0.6 mm thick), the Si_3N_4 and Mo discs were bonded in vacuum 1.3×10^{-3} Pa at 1 273 K for 3.6 ks under an applied pressure of 9.8 MPa.

A transmission electron microscope (TEM) with high resolution capabilities, JEM-200CX operating at 200 kV, was used for the cross-sectional observation of the interface. The cross-sectional specimens were

prepared by ion thinning with an acceleration voltage of 5 kV. Some samples were examined in a JEM-4000EX microscope operating at 400 kV for the purpose of high-resolution observation of thicker interfaces. With a beam size of 30 nm, local structural and elemental analyses with micro-area electron diffraction and energy dispersive X-ray spectroscopy (EDS) were made by using analytical TEM, JEM-2000FX. Compositional profiles across the Si_3N_4 interface were calculated from data obtained by an Auger electron spectroscope (AES), JAMP-30, with a primary electron beam of 200 nm in diameter and an acceleration voltage of 6 kV.

For the sake of generality in the results, also supplemental experiments with X-ray diffraction were carried out. In obtaining a high volume fraction of reaction products for X-ray diffraction analysis, mixtures of α - Si_3N_4 and high purity Ni powders were compacted in a cold isostatic pressing (CIP) machine and annealed at 1 173 and 1 273 K followed by oil quenching, to prevent any solid-state reaction which could take place during slow cooling or by furnace cooling. Conventional powder X-ray diffraction was used in the analysis of the compacted bodies.

3. Results

Before going into detailed electron microscopic studies, compositional profiles of the possible diffusion elements across the bonded interface were obtained by the analysis of a micro-AES data, in order to know the extension of the reaction area at the bonded interface. Fig. 2 shows the calculated compositional profiles of Si, N, O and Ni across the boundary. The sensitivity factor used in the composition profile calculations were corrected to fit the nominal composition of Si_3N_4 . In Fig. 2, Si and N diffuse in a similar way towards the Ni side, after the decomposition of Si_3N_4 . However, the Ni and Si profiles do not present the plateau characteristic of the presence of compounds such as silicides. A layer of about 2 μm thick between Ni and Si_3N_4 is considered to be a reaction layer of Ni alloy with Si and N in solid solution. However, a silicide layer thinner than the

Fig. 2. Calculated AES compositional profiles for the principal elements across the interface.

probe diameter could be undetectable. The oxygen distribution across the interface reveals a relatively high oxygen content in the ceramic. This is attributed to the presence of oxide additives of MgO and Al_2O_3 and free oxygen at the grain boundaries. The oxygen is considered to diffuse toward the metal side as it is proved by the compositional profile. A possible reaction between O and Si to form some kind of amorphous phase should not be disregarded.

A cross-sectional observation of the interface made by TEM revealed that Si_3N_4 and polycrystalline Ni are in intimate contact.²⁾ However, in the Ni side, void formation was observed at a distance about 2 μm of the interface. These voids are the result of mass transfer of Ni towards Si_3N_4 after its decomposition at the bonding temperature in vacuum and could be considered as the markers of the original interface position. The most important feature was the apparent absence of a third phase different from the Ni or the Si_3N_4 . No special crystallographic orientation relationship was found between Si_3N_4 and Ni. This was confirmed by taking diffraction patterns from the two structures in several different areas.

We have applied high-resolution electron microscopy to study the cross section of the interfaces from several different specimens and have proved beyond doubt that silicide phases are missing at the interface. Fig. 3 is an example of high resolution image taken with a TEM operating at 200 kV. The beam incidence is parallel to [0001] of Si_3N_4 . Crossed lattice fringes of (10 $\bar{1}$ 0) and (01 $\bar{1}$ 0) lattice planes of Si_3N_4 are observed together with lattice fringes of (111) Ni plane. No other phase is observed at the interface. A dark contrast region at the boundary is certainly due to the presence of internal stresses generated within the interface of two dissimilar compounds. In the Ni region close to the boundary, we often observe locally discontinuous lattice images which are due to dislocations densely formed. The dislocation density in this area was estimated to be nearly equal to $1 \times 10^{11}/\text{cm}^2$. In this study, no interfacial images could be obtained from really flat interfaces, which are exactly parallel to the beam, and an overlapping of lattice fringes at the interface could not be avoided as seen in Fig. 3. Here, white lines indicated at the boundary as continuation of fringes of Ni and Si_3N_4 show the overlapping of lattice fringes. No fringes for a third phase are present at the boundary region.

Fig. 4 shows a high-resolution micrograph near the region of Fig. 3 taken by tilting the specimen about 7°. In this case, the beam is parallel to [123] of Ni. In Fig. 4, a fine granular contrast typical of the amorphous structure can be seen at the area indicated by arrows. Such area must be related to the local formation of an amorphous phase, SiO_2 or free Si. It was found that such amorphous-like contrast was rarely observed at the interfaces in the present specimens.

High-resolution images at a thicker region of the interface were obtained by using a TEM operated at 400 kV. Fig. 5 shows a lattice image at the interface area taken at 400 kV. No third phase, including

amorphous phase, is observed at the boundary region even at the thicker part of the specimen. Coarse fringes parallel to the grain boundary are extinction fringes of Ni (or Ni alloy). Dislocations are also observed in the Ni side.

In the lattice imaging technique, because of the formation of moiré fringes and localized lattice strain contrast, a possible third phase as small as several nanometers can not be clearly imaged when the phase is overlapped with Si_3N_4 or Ni phases at the boundary. By conventional selected area diffraction information from areas as wide as 300 nm in diameter is obtainable. However, micro-diffraction analysis with a micro-electron beam gives the very local information that is required to elucidate whether a certain third phase is present or not at the interface region. In Fig. 6 an example of the micro-beam diffraction patterns is shown together with the high-resolution lattice image of Si_3N_4 and Ni of the interface area. The micro-beam used was about 30 nm in diameter. It was found that the electron diffraction pattern at the interface (Fig. 6(c)) is not more than the superposition of diffraction patterns for Si_3N_4 (b) and Ni (or Ni alloy) (a) in the analyzed area. A halo diffraction pattern as the evidence of amorphous phase could not be observed in the present micro-beam analysis.

Micro-beam EDS analysis confirmed the AES results. In Fig. 7 a scheme for the analysis mode and its results are presented. Silicon content is found to decrease progressively as the distance from the interface increases, in a similar tendency as the observed for AES data. However, no quantitative on the diffusion length for Si and N was obtained. Species such as Mg and Al, which are included in the Si_3N_4 grain boundaries, do not take part in the diffusional processes towards Ni as it reveals the absence of signal for these elements in the EDS spectra. Equipment limitations did not allowed the analysis of a small amount of light elements, but there is no reason to assume the results different from the AES analysis.

4. Discussion

Detailed high-resolution and analytical TEM studies together with the AES analysis showed no evidence of any interfacial reactions of silicide formation, except a reaction to form a Ni-Si-(N) solid solution. As it was mentioned in Introduction, there are two mechanisms which tentatively explain the Si_3N_4 -Ni interface reaction. However, the process which considers the existence of a melt phase at the interface (model I) is inconsistent with the TEM results obtained in this study.

Considering the reaction between Si_3N_4 and Ni under high temperature and high vacuum conditions, some authors adopt the simple binary Ni-Si phase diagram. The reaction between Si_3N_4 and Ni has been explained in terms of an eutectic melt formation.^{6,7)} Although no explicit mention was made of the compound involved in the referred eutectic reaction, the NiSi is the compound with a low-eutectic point (1 273 K) for this system in accordance with the

Fig. 3. Lattice image of the Si_3N_4 -Ni interface taken with electron beam parallel to $[0001]$ of Si_3N_4 . Electron diffraction patterns for both Si_3N_4 and Ni are shown in the insets.

Fig. 4. Lattice image of the Si_3N_4 -Ni interface taken with electron beam parallel to $[123]$ of Ni. Electron diffraction patterns for both Si_3N_4 and Ni are shown in the insets.

Fig. 5. Lattice image of thicker region of the interface taken by a JEM-4000EX operated at 400 kV. Electron diffraction pattern for Si₃N₄ is shown in the inset.

Fig. 6. Micro-area electron diffraction patterns do not reveal the presence of a third phase different from Ni or Si₃N₄ at the interface.

Fig. 7. EDS analysis mode and the results for Ni and Si across the interface.

Fig. 8. X-ray diffraction patterns for different heat treatments of CIP compacted powders. No lines for the compound NiSi could be found.

available phase diagram.⁸⁾ However, no evidence for the presence of this compound at the interface could be obtained in the present study. Then, it seems important to elucidate, if NiSi could be formed in the reaction between Si₃N₄ and Ni. Therefore, the supplemental work with reacted powders, mentioned

above, was carried out.

Fig. 8(a) shows the X-ray diffraction lines for the sample quenched from 1 173 K; stronger lines for Ni and α - Si_3N_4 are observed and no evidence of any silicide formation was found in this pattern. This result corroborates the fact that no silicide reaction, in this system, is preceded by the decomposition reaction of Si_3N_4 in vacuum. In Fig. 8(b) the results for the specimen quenched from 1 273 K are presented. Here in contrast with Fig. 8(a), clearly distinguishable lines for $\text{Ni}_{31}\text{Si}_{12}$ and a marked broadening of Ni peaks were found, revealing the presence of Ni_3Si , named β_1 . In the same way, strong reflections for the β_2 - Ni_3Si were identified. When the heat treated specimen is cooled down slowly, *e.g.*, furnace cooled, a further change takes place. Fig. 8(c) indicates that the low temperature stable Ni-rich silicides remain after slow cooling from 1 273 K. β_2 -phase is a metastable phase, and it tends to disappear at lower temperatures. From Fig. 8, the most important result is the total absence of NiSi reflections. This proves in a very simple way that this compound is not formed during the reaction of Si_3N_4 with nickel at the temperatures of interest, even in the case of powder reaction where silicides formation occur easily. A diffraction pattern for the phase of interest, NiSi, is not available in the set of standard power diffraction patterns, and we found difficulties in indexing experimental patterns of our standard NiSi powders with the spacing calculated from the published lattice parameters of single crystals ($a=0.518$ nm, $b=0.334$ nm and $c=0.562$).⁹⁾ d'Heurle *et al.*,¹⁰⁾ in a recent paper dealing with the formation of thin films of NiSi, have calculated all lattice spacings and intensities according to the relative atomic positions given in Ref. 9) (NiSi is orthorhombic of space group Pnma) but with a newly proposed unit-cell dimensions ($a=0.5233$ nm, $b=0.3258$ nm and $c=0.5659$ nm). The fit between this calculated data and our standard powders results was quite good and the evaluation of NiSi, in the reacted powders, was made by using this calculated data.

According to the Ni-Si phase diagram, the Ni-richest phase is Ni_xSi (β_1 -phase), where x is about 3.6.¹¹⁾ This phase is commonly referred to as Ni_3Si with the Cu_3Au I type of structure and it is thermodynamically the most stable nickel silicide. We could not obtain any evidence of the ordered or partially ordered Ni_3Si phase in the Ni phase region close to the interface boundary from electron diffraction data.

In the model II of Fig. 1, we proposed the possibility of a Ni_3Si or face centered cubic Ni-Si-N solid solution as the final reaction phase. However, the electron diffraction results mentioned above exclude the possibility of the Ni_3Si formation.

5. Conclusions

We have combined high resolution electron micro-

scopy and analytical electron microscopy including micro-area electron diffraction in a detailed local structural analysis of the interface of bonded Si_3N_4 -Ni.

No nickel silicide as a reaction product was present at the interface and a simple solid-state reaction mechanism (model II in Fig. 1) was proved to be the possible mechanism in the present Si_3N_4 -Ni interface reaction at 1 273 K in high vacuum. In accordance with this mechanism, Si_3N_4 reacts with Ni to produce as a unique product of reaction a Ni-Si-N solid solution.

The melt-like region we observed previously at the interface in the high temperature optical microscope²⁾ should be considered as a result of mass-transfer process due to Ni diffusion towards Si_3N_4 side immediately after the decomposition of the nitride. It was demonstrated by supplemental X-ray work that formation of NiSi phase does not take place easily during the reaction of Si_3N_4 and Ni in vacuum at 1 273 K.

Acknowledgements

This work was supported in part by a cooperation program of The Ministry of Education, Science and Culture of Japan and NKK Corp. Thanks are also due to JEOL, Ltd. for permitting the use of their facilities. We would like to thanks Prof. S. Nagakura, Nagaoka University of Technology, for helpful discussions and continuous encouragement. One of the authors (M.E.B.), further acknowledges the scholarship granted by The Ministry of Education, Science and Culture of Japan.

REFERENCES

- 1) for example, T. Yamada, S. Kitamura and E. Sekiguchi: Proc. of 2nd Int. Symp. on Ceramics Materials and Components for Engines, ed. by W. Bunk and H. Hausner, Verlag Deutsche Keramische Gesellschaft, (1986), 441.
- 2) M. E. Brito, H. Yokoyama, Y. Hirotsu and Y. Mutoh: Proc. MRS Int. Symp. on Advanced Materials, ed. by M. Doyama and S. Somiya, Tokyo, (1988), to be published by Mater. Res. Soc., Penn.
- 3) L. F. Voitovich: Refractory Compounds, Naukovy Dumka, Kiev, (1971), 96.
- 4) W. B. Wincke and L. R. Bratley: *J. Am. Chem. Soc.*, **52** (1930), 48.
- 5) K. Suganuma, T. Okamoto, Y. Miyamoto, M. Shimada and M. Koizumi: *Mater. Sci. Technol.*, **2** (1986), 1156.
- 6) M. Nakahashi, M. Shirokane and H. Takeda: *HYOMEN (Surface)*, **24** (1986), 595.
- 7) K. Suganuma, Y. Miyamoto and M. Koizumi: *Ann. Rev. Mater. Sci.*, **18** (1988), 47.
- 8) Metals Handbook, 8th ed, Vol. 8, Am. Soc. Metals, Metals Park, Ohio, (1973), 325.
- 9) K. Toman: *Acta Crystallogr.*, **5** (1952), 329.
- 10) F. d'Heurle, C. S. Petersson, J.E.E. Baglin, S. J. La Placa and C. Y. Wong: *J. Appl. Phys.*, **55** (1984), 4208.
- 11) M. Bartur and M. A. Nicholet: *J. Appl. Phys.*, **54** (1983), 5404.