

# Joining of $\text{Si}_3\text{N}_4$ to $\text{Si}_3\text{N}_4$ using a $\text{AuPd}(\text{Co}, \text{Ni})\text{--V}$ filler alloy and the interfacial reactions

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## Abstract

$\text{Au}38.0\text{--Pd}28.0\text{--Co}18.0\text{--Ni}7.0\text{--V}9.0$  (in wt%) alloy was designed as a filler for joining  $\text{Si}_3\text{N}_4$ . The filler alloy showed a contact angle of  $77.2^\circ$  on  $\text{Si}_3\text{N}_4$  ceramic at 1473 K. The  $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$  joint brazed with the rapidly-solidified filler foils at 1443 K for 10 min exhibits an average three-point bend strength of 320.7 MPa at room temperature and the strength values are 217.9 MPa and 102.9 MPa at 1073 K and 1173 K respectively. The interfacial reaction products were composed of  $\text{V}_2\text{N}$  and  $\text{Pd}_2\text{Si}$ , and the elements Co and Ni in the brazing alloy did not participate in the interfacial reactions. The coarse-network-like distribution of refractory  $\text{Pd}_2\text{Si}$  compound within the  $\text{Au}\text{--Pd}\text{--Co}\text{--Ni}$  alloy matrix throughout the joint contributes to the stable high-temperature joint strengths.

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## 1. Introduction

The wettability of traditional brazes on ceramics is not good due to the fact that there exists a great difference in physical and chemical properties between ceramic and metal. Therefore active brazing technique has been developed for ceramic joining, in which elements Ti, Zr, Cr and V are often used as the active element in brazing alloys for inducing wetting with ceramic. It is well known that  $\text{AgCu}\text{--Ti}$  filler alloy is the most commonly used active brazing alloy, and when it is used for  $\text{Si}_3\text{N}_4$  joining, the resulting reaction products of  $\text{TiN}$  and  $\text{Ti}\text{--Si}$  compounds are necessary for interfacial bonding. However, the  $\text{AgCu}\text{--Ti}$  alloy's service temperature is too low. Therefore, since the 90s in the last century, development of new high-temperature brazes for the joining of ceramic to ceramic and ceramic to metal had become a research focus.

$\text{Ni}\text{--Cr}\text{--Si}$  system alloy was used as brazing filler for  $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$  joining, and four-point bend strength of the corresponding joints at room temperature was low, only 118 MPa [1]. Some researchers made attempts to join  $\text{Si}_3\text{N}_4$  ceramic by

using  $\text{Ni}\text{--Cr}\text{--Si}\text{--Ti}$  and  $\text{Co}\text{--Ti}$  as brazes [2,3], but the results were not satisfactory. The fact that, the element Ti has a large affinity with Ni or Co, so the active element Ti strongly combines with elements Ni or Co and forms stable compounds, and this would limit the actual activity of Ti in the Ni- or Co-based brazing alloys, explains why it is difficult to join  $\text{Si}_3\text{N}_4$  by directly using the previously mentioned Ti-active Ni (Co)-based brazing alloys. Some other researchers designed brazing alloys containing noble metal Au for  $\text{Si}_3\text{N}_4$  joining, such as  $\text{Au}82.1\text{--Ni}15.5\text{--V}1.7\text{--Mo}0.7$  (wt%),  $\text{Au}\text{--}8\text{Pd}\text{--}3$  to  $4\text{V}$  (wt%) and  $\text{Au}78.7\text{--Ni}15.6\text{--Pd}3.9\text{--V}1.8$  (wt%) alloys [4–6], in which the amount of Au is more than 78.0 wt% and V were used as active element, and the bend strengths of the  $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$  joints at room temperature are about 260–350 MPa. However, the corresponding high-temperature joint strength is not satisfactory, for example, the joint strength at 1073 K is less than 100 MPa [4], and, at 1173 K it even shows an extremely low value of 13 MPa [6]. Therefore, searching for new high-temperature brazes with not only low cost but also an improved joint strength for  $\text{Si}_3\text{N}_4$  joining should be of great significance.

Sound  $\text{Si}_3\text{N}_4/\text{Mo}$  joints or  $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$  joints have been achieved using vanadium foil [7] or V-containing filler metals

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[4–6,8], the reactions between V-containing metals and  $\text{Si}_3\text{N}_4$  ceramic are dependent on the metals' composition and heating condition, and therefore the corresponding reaction products are different from each other under different reaction conditions. However, so far, the understanding of the interfacial reactions between V-active brazes and  $\text{Si}_3\text{N}_4$  ceramic are far insufficient, and moreover, the relationship between the reaction products at the interface and the high-temperature joint strength remains to be clarified.

The objective of this study was to use a high temperature brazing technique for joining of  $\text{Si}_3\text{N}_4$  to  $\text{Si}_3\text{N}_4$  using a new brazing alloy. Elements Co, and Ni are commonly-used primary constituents in commercial superalloys, and thus Co (Ni)-based alloy matrix should have superior high-temperature properties. But our previous study results indicated that Ni–V, Co–V, and Ni–Cr–V system brazing alloys had no potential possibility as filler metal for  $\text{Si}_3\text{N}_4$  joining as the reactions between those alloys and the  $\text{Si}_3\text{N}_4$  at high temperatures were too intensive [9].

As described previously, it has been demonstrated that the active effect of element V in  $\text{Si}_3\text{N}_4$  joining is good in Au-based alloys and suitable reactions have been induced at the interfaces [4–6]. Additionally, Pd possesses good thermal and oxidation resistance, and Pd-based filler metals have been primarily investigated [10–12]. Therefore, it can be deduced that Au–Pd–V ternary alloys should be good high-temperature filler candidates for  $\text{Si}_3\text{N}_4$  joining. However it is well known that too-high liquidus temperature of the filler alloys should be avoided, especially for ceramic joining. According to Au–Pd system binary diagram, when Pd amount is more than 7.0 wt% in Au–Pd alloys, the alloys' liquidus temperatures would exceed 1473 K, and when the Pd amount reaches 15.0 wt%, the liquidus temperature would be steeply increased to above 1573 K [13]. This means that if we only design a Au–Pd–V ternary alloy with a liquidus temperature of no higher than 1473 K, the addition amount of Pd should be probably with a rather low level, and this will undoubtedly limit its high-temperature property advantage. Now, in this study, one new Au-based brazing alloy, AuPd(Co, Ni)–V, was designed. In our design, Pd and Co+Ni with rather high concentrations were added into the Au-based alloy, and this was a result of the following two considerations. (i) Elements Co and Ni, when added into Au–Pd–V alloy, because of those eutectic reactions between them and element V [13], would decrease the liquidus temperature of the Au–Pd–V master alloy. Furthermore, there monotonously exists a composition point where the melting temperature is the lowest for each one of Co–Pd, Ni–Pd, Au–Co, and Au–Ni binary systems [13]. The previous two factors make it possible to acquire some AuPd(Co, Ni)–V alloys with suitable liquidus temperatures. (ii) It has been recognized that element Pd has a large affinity with Si [14–17]. When Pd with a rather high concentration is added into the brazing alloy, during the brazing process Pd atoms would react with Si atoms decomposed from  $\text{Si}_3\text{N}_4$ , resulting in the formation of Pd–Si compounds with a considerable amount within the  $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$  joint. It is believed that the refractory Pd–Si compound formation is favorable to the joint strength and high-temperature stability.

In the present paper the authors proposed one AuPd(Co, Ni)–V brazing filler alloy, in which the Au content was only 38.0 wt%. Presently the price of metal Pd is much lower than that of Au. Then, compared with those previously reported Au-based V-active filler metals, the newly-designed AuPd(Co, Ni)–V brazing alloy will undoubtedly possess an advantage of low cost.

In the present study, we conducted a wetting experiment of the AuPd(Co, Ni)–V brazing alloy on  $\text{Si}_3\text{N}_4$  ceramic. Then, the new brazing alloy was fabricated into rapidly-solidified foils for the use of  $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$  joining. This study was intended to address the questions of what reactions would result at the interface using AuPd(Co, Ni)–V brazing alloy, whether the formation of Pd–Si compounds with a considerable amount can be induced within the  $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$  joint, and whether the newly-developed brazing alloy can offer a stable high-temperature strength for the  $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$  joints.

## 2. Experimental procedure

We designed a new filler alloy, with a composition of Au38.0–Pd28.0–Co18.0–Ni7.0–V9.0 (in wt%). The brazing alloy was fabricated into brazing foils with a thickness of about 50  $\mu\text{m}$  by the following rapidly-solidifying technique: double melting the AuPd(Co, Ni)–V master alloy from high-purity metals of Au, Pd, Co, Ni and V; smashing the master alloy to pieces and melting them again in a silica tube by induction heating in a vacuum chamber; finally, turning off the vacuum system, and by putting high-purity argon (99.999%) into the silica tube, ejecting the liquid alloy from the bottom of the silica tube onto the outer surface of a copper wheel rotating at 1800 rpm. Hot-press sintered  $\text{Si}_3\text{N}_4$  ceramics, with totally 12 wt%  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  as sintering aid, were used as the joined material. The ceramic surface was polished by 1000# SiC sand paper and subsequent diamond paste with a size of 1.0  $\mu\text{m}$  so that it showed a mirror-bright surface. The used brazing filler foils and the  $\text{Si}_3\text{N}_4$  samples were ultrasonically cleaned in acetone and dried by air blowing.

The wettability of the AuPd(Co, Ni)–V brazing alloy on  $\text{Si}_3\text{N}_4$  was studied with the sessile drop method. The brazing alloy sample with a diameter of about 5 mm and a weight of about 100 mg was placed on a  $\text{Si}_3\text{N}_4$  ceramic substrate with a size of  $10 \times 10 \times 2 \text{ mm}^3$ . The chamber of the furnace was first evacuated to  $1.5 \times 10^{-3} \text{ Pa}$  by a mechanical rotatory pump and molecule pump at room temperature. Then, the vacuum system was turned off, and high-purity (99.999%) argon was put into the chamber with a pressure of 0.1 MPa. Subsequently the chamber was evacuated to  $1.5 \times 10^{-3} \text{ Pa}$  again, the vacuum system was turned off, and argon was put into the chamber for the second time. The brazing alloy sample was heated to 1473 K from ambient temperature at a heating rate of 8–10 K/min, and was held at this temperature for 10 min. During the heating process, the morphologies of the molten droplet were recorded dynamically by taking sideways photos at intervals when heating and holding at the temperature of 1473 K. The contact angles of the brazing alloys on the ceramic were thus calculated from those droplet images using

computer method based on the Laplace equations [9]. The accuracy of the contact angle measurements should be within  $\pm 1^\circ$ .

The samples to be brazed were vertically fixed in a specially designed graphite jig (shown in Fig. 1) to form a butt joint. The size of the  $\text{Si}_3\text{N}_4$  bars to be joined is  $3 \times 4 \times 20 \text{ mm}^3$ . The heating rate of the brazing experiment was 15 K/min. Four brazing temperatures were chosen, and brazing time was fixed at 10 min. During the brazing experiment a pressure of about 0.05 MPa was applied upon each joint and the vacuum was kept between  $3.0 \times 10^{-3} \text{ Pa}$  and  $7.0 \times 10^{-3} \text{ Pa}$ . After brazing the cooling rate was 15 K/min down to 673 K, then about 3 K/min to room temperature. The as-brazed butt joints were directly subjected to a three-point bend test. The joint strength was determined by the bend test at room temperature and at high temperatures. Five specimens were tested for each experimental condition, and the joint strength is given in the form of error bars, in which the value of the upper line is the maximum strength among the five specimens, the value of the lower line corresponds to the minimum strength, and the point in the middle of the error bar represents the average strength.

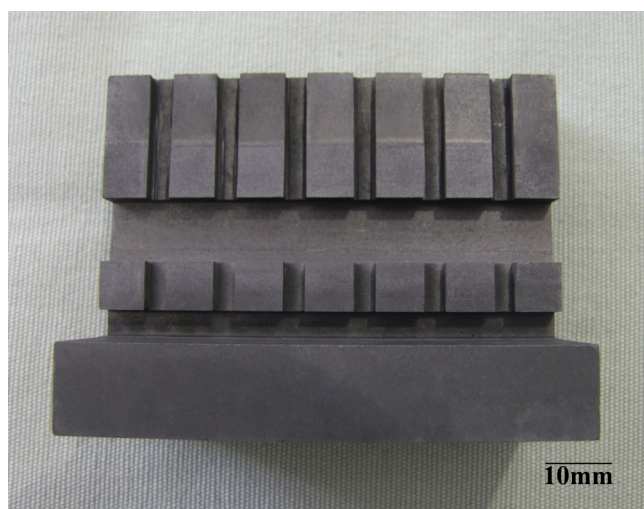


Fig. 1. Graphite jig used to form butt joint.

A JEOL-5600LV (Akishima city, Japan) type scanning electron microscope (SEM) was used for microstructure observation of the brazed joint. Furthermore, an Oxford Inca type X-ray energy-dispersive spectrometer (XEDS) was used for semi-quantitative composition analysis of some typical microzones at the interface. For better phase identification of the  $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$  joint, X-ray diffraction (XRD) analysis was performed on a simulated specimen of the  $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$  joint brazed at 1443 K/10 min. The simulated specimen was prepared by the following process: 0.12-mm-thickness alloy plate was prepared by spark cutting and surface polishing from the AuPd(Co, Ni)–V brazing alloy ingot, and it was placed on a  $\text{Si}_3\text{N}_4$  sample with a size of  $8 \times 8 \times 2 \text{ mm}^3$ ; then, they were put in a vacuum furnace, heated to 1443 K and held there for 10 min, followed by a slow cooling. Subsequently, the unreacted brazing alloy at the outermost surface of the  $\text{Si}_3\text{N}_4$  sample was moved away and gradual polishing was conducted through the reaction zone at the sample surface, and XRD analysis was carried out successively on the surface step by step.

### 3. Results and discussions

According to a differential thermal analysis (DTA) result, the liquidus temperature of the AuPd(Co, Ni)–V alloy is 1422.3 K. It was found that, once the AuPd(Co, Ni)–V alloy melted on the surface of the  $\text{Si}_3\text{N}_4$ , it showed a contact angle of  $90.0^\circ$ , and with the increase of the temperature, the contact angle became smaller gradually, indicating wetting with  $\text{Si}_3\text{N}_4$ . When the alloy sample was heated to 1473 K, its contact angle was decreased to  $77.2^\circ$  (Fig. 2(a)). But, as shown in Fig. 2(b), with the prolonging of the holding time at 1473 K, the contact angle only fluctuated slightly, without further decreasing. Fig. 3 shows the morphology of AuPd(Co, Ni)–V alloy molten droplet on  $\text{Si}_3\text{N}_4$  after being held at 1473 K for 10 min.

The rapidly-solidified brazing foils were used in the subsequent brazing experiment. The results indicate that the  $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$  joints brazed at 1423 K for 10 min exhibited an average three-point bend strength of 298.3 MPa at room temperature, and the average joint strength was elevated to 320.7 MPa when the brazing temperature was increased to

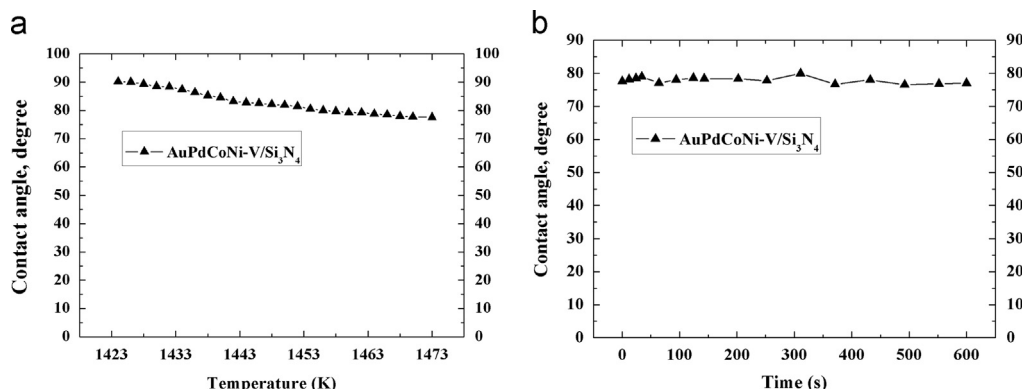


Fig. 2. Wetting kinetics of the AuPd(Co, Ni)–V alloy on  $\text{Si}_3\text{N}_4$ . (a) Change of contact angle with temperature and (b) change of contact angle with holding time at 1473 K.



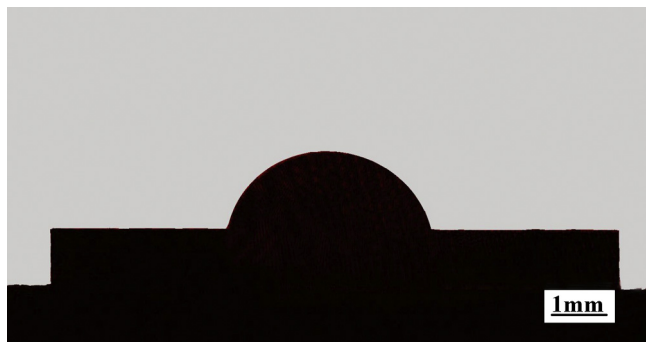


Fig. 3. Morphology of AuPd(Co, Ni)-V molten droplet on  $\text{Si}_3\text{N}_4$  (1473 K for 10 min).

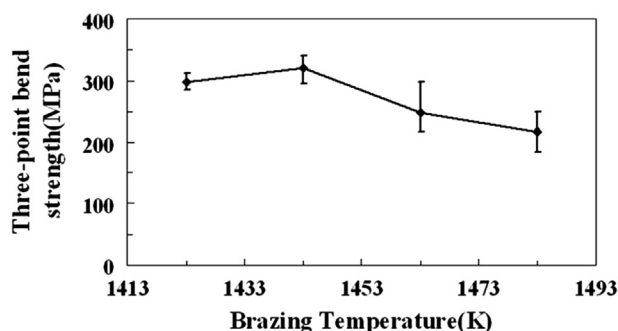


Fig. 4. Effect of brazing temperature on joint strength (Brazing filler: AuPd(Co, Ni)-V foil; brazing time: 10 min.).

1443 K, as shown in Fig. 4. When the brazing temperature was further increased, the joint strength was conversely decreased, that is, at brazing temperature of 1483 K, the joint strength was decreased to 225.3 MPa.

Fig. 5 presents back scattered electron images of the  $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$  joint brazed with the AuPd(Co, Ni)-V filler foils at three brazing temperatures of 1423 K, 1443 K, and 1483 K. The joint microstructures appear non-homogeneous. Careful microstructure observation was conducted on the joint brazed at 1443 K. Two reaction bands, with a thickness of about 3  $\mu\text{m}$ , should have been formed at the two interfaces close to  $\text{Si}_3\text{N}_4$  (marked microzone “1” in Fig. 5(b)). According to the XEDS analysis results shown in Table 1, the corresponding reaction product should be V-N compound. Fig. 6(a) also infers the strong enriching phenomenon of the element V at the interface. Moreover, in the central part of the brazed joint, the phases should be composed of residual brazing alloy (microzones “2” and “3” in Fig. 5(b)) and Pd-Si compound (microzone “4” and “5” in Fig. 5(b)). It is noticeable that the distribution map of element Pd is in good agreement with that of Si (Fig. 6(b) and (c)), indicating the presence of Pd-Si compound throughout the joint. In the Pd-Si microzones elements Au, Co Ni and V are hardly detectable (Table 1). It appears that the residual brazing alloy and Pd-Si compound distribute separately to each other, and this point is also demonstrated by the element distribution maps (Fig. 6(b)–(f)). Here, the residual brazing alloy in the joint is characterized by an eutectic microstructure

(microzones “2” and “3” in Fig. 5(b)), showing an Au-Pd-Co-Ni alloy's composition (Table 1).

The XRD results verify that the interfacial reaction products are composed of  $\text{V}_2\text{N}$  and  $\text{Pd}_2\text{Si}$ , shown in Fig. 7, in which three different JCPDS cards were used as standard file for the determination of different phases [18–20]. The element V was hardly detectable in the residual brazing alloy, signifying that the activity of V is strong in the AuPd(Co, Ni)-V system alloy and the V in the brazing alloy had been consumed almost completely by the formation of the two  $\text{V}_2\text{N}$  bands through the interfacial reactions. Obviously, the  $\text{V}_2\text{N}$  compound distributed at the interfaces close to the  $\text{Si}_3\text{N}_4$  (Fig. 5 (b)), while the  $\text{Pd}_2\text{Si}$  compound formed not only at the interface adjacent to the  $\text{V}_2\text{N}$  reaction bands but also within the residual brazing alloy, exhibiting a coarse-network-like distribution throughout the  $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$  joint brazed at 1443 K for 10 min.

The coarse-network-like distribution of Pd-Si compound is also visible throughout the  $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$  joint brazed at 1423 K. But for the joint brazed at 1483 K, the corresponding joint microstructure becomes more non-homogeneous. The evident decrease of the strength of the joint brazed at 1483 K (Fig. 4) should be attributed to this change of the joint microstructure.

The chemical reactions at high temperatures between  $\text{Si}_3\text{N}_4$  and element V are complex, so that different reaction products have been reported in some references under different experimental conditions. For example, M. Paulasto et al. reported the formation of  $\text{VN}_x$  under the condition of 1273 K/30 min in Ar at  $\text{Si}_3\text{N}_4/\text{Au-Ni-V-Mo}$  interface, and no V-silicides were found at the interface [4]. However, conversely, in the system of  $\text{Si}_3\text{N}_4/\text{V/Mo}$  under a bonding condition of 1328 K/90 min/20 MPa only  $\text{V}_3\text{Si}$  was formed at the interface, and no vanadium nitride was found [7]. Moreover, when the bonding temperature was increased to 1523 K, in addition to  $\text{V}_3\text{Si}$ , another silicide  $\text{V}_5\text{Si}_3$  was formed at the interface.

But M. Maeda et al. reported that in the system of  $\text{Si}_3\text{N}_4/\text{V}/\text{Si}_3\text{N}_4$  under a bonding condition of 1473 K/60 min/140 MPa, the compounds of  $\text{V}_3\text{Si}$  and  $\text{V}_2\text{N}$  were concurrently formed at the interface, and with the increase of bonding temperature and the prolonging of bonding time, besides  $\text{V}_3\text{Si}$  and  $\text{V}_2\text{N}$ , new reaction products of  $\text{V}_5\text{Si}_3\text{N}_{1-x}$  and VN appeared in the joint [21].

Additionally, according to the estimation of T. Sera et al., after brazing at 1423 K for 5–15 min using Al-V-Ni-Cu filler metal the reaction products of V-Ni-Si,  $\text{V}_2\text{N}$  and VN should have been formed at the interface close to  $\text{Si}_3\text{N}_4$  [8]. In our previous study  $\text{V}_3\text{Ni}_2\text{Si}$ ,  $\text{V}_6\text{Si}_5$  and VN were formed under the heating condition of 1553 K/120 min for the reaction system of  $\text{Si}_3\text{N}_4/\text{Ni-V}$  alloy [9]. In these cases, the element Ni also participated in the interfacial reactions.

However, in the present study,  $\text{V}_2\text{N}$  and  $\text{Pd}_2\text{Si}$  were detected as the reaction products at the interface, and it appeared that under the brazing condition of 1443 K/10 min the elements Co and Ni in the brazing alloy did not participate in the interfacial reactions at all. Furthermore, V-Si compounds were not detectable at the interface.

Therefore, we can speculate that at high temperatures, active element V would firstly diffuse from the AuPd(Co, Ni)-V

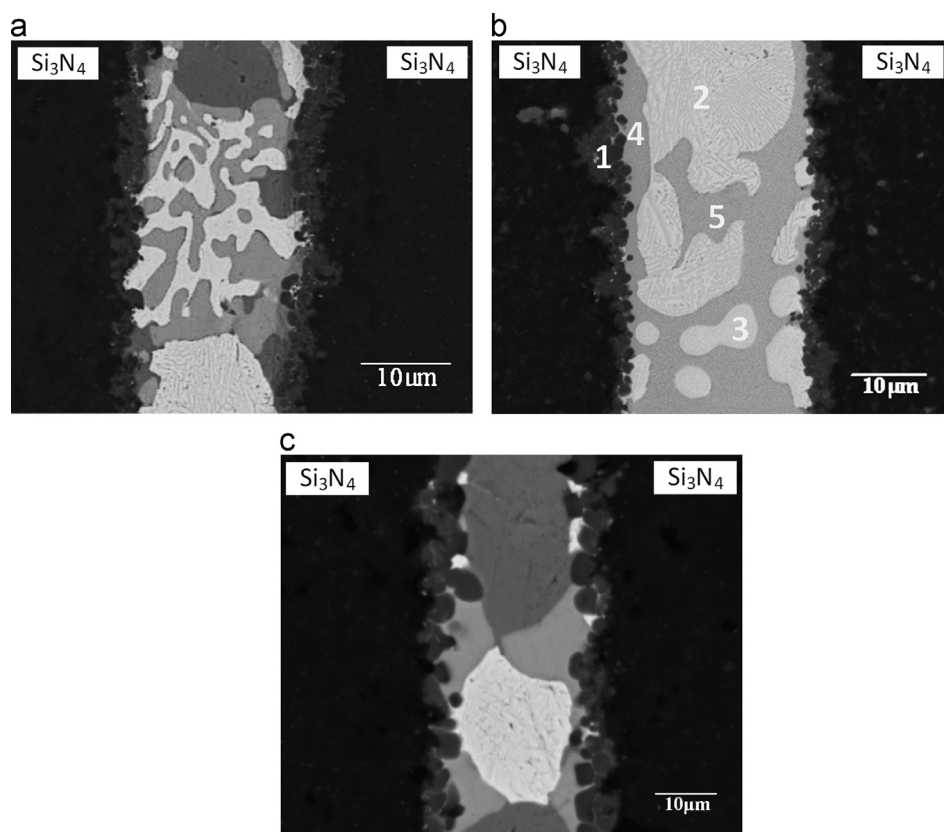


Fig. 5. Back scattered electron images (BSEI) of  $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$  joint brazed at different temperatures (Brazing time: 10 min) (a) 1423 K; (b) 1443 K; and (c) 1483 K.

Table 1

XEDS analysis results of microzones marked in Fig. 5(b).

Microzones	Concentration, at%								Deduced phases
	N	Si	V	Co	Ni	Pd	Au	Total	
Reaction Microzone “1”	23.22	3.75	67.27	2.76	1.38	0.94	0.68	100.00	V–N compound
Greyish white microzone “2”	–	–	0.57	23.69	10.29	26.61	38.84	100.00	Au–Pd–Co–Ni alloy
Greyish white microzone “3”	–	–	0.74	22.74	12.76	27.17	36.59	100.00	Au–Pd–Co–Ni alloy
Gray microzone “4”	–	29.23	–	0.61	1.85	67.61	0.70	100.00	$\text{Pd}_2\text{Si}$ compound
Gray microzone “5”	–	30.71	0.66	–	1.55	66.49	0.60	100.00	$\text{Pd}_2\text{Si}$ compound

brazing alloy to the surface of  $\text{Si}_3\text{N}_4$ , and react with  $\text{Si}_3\text{N}_4$  through the following formula:



Then, usually, at high temperatures the Si atoms released from  $\text{Si}_3\text{N}_4$  would diffuse into the brazing alloy where they would further react with the elements Pd, Co, Ni and V in the alloy, to precipitate Pd–Si, Co–Si, Ni–Si and V–Si compounds. However, in our experiment, among the previous four kinds of silicides only Pd-silicide was detectable (microzones “4” and “5” in Fig. 2(a)). The reaction for the formation of Pd-silicide at the interface can be expressed by the following equation:



Dissolution enthalpies of element Si in melts of Au, Pd, Ni, Co and V are  $-48$  kJ/mol,  $-145$  kJ/mol,  $-98$  kJ/mol,  $-91$  kJ/mol, and  $-128$  kJ/mol [22], signifying that the combining capacity of Pd with Si should be the strongest among the five elements in the AuPd(Ni, Co)–V brazing alloy. This explains the reason why the formation of  $\text{Pd}_2\text{Si}$  is intensive whereas other silicides are absent within the brazed joint. Therefore the overall reaction during the brazing process can be summarized as the following equation:



For the  $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$  joints brazed at 1443 K for 10 min, when tested, cracking originated from the brazed interface and propagated to both sides, as shown in Fig. 8(a) and (b), and a

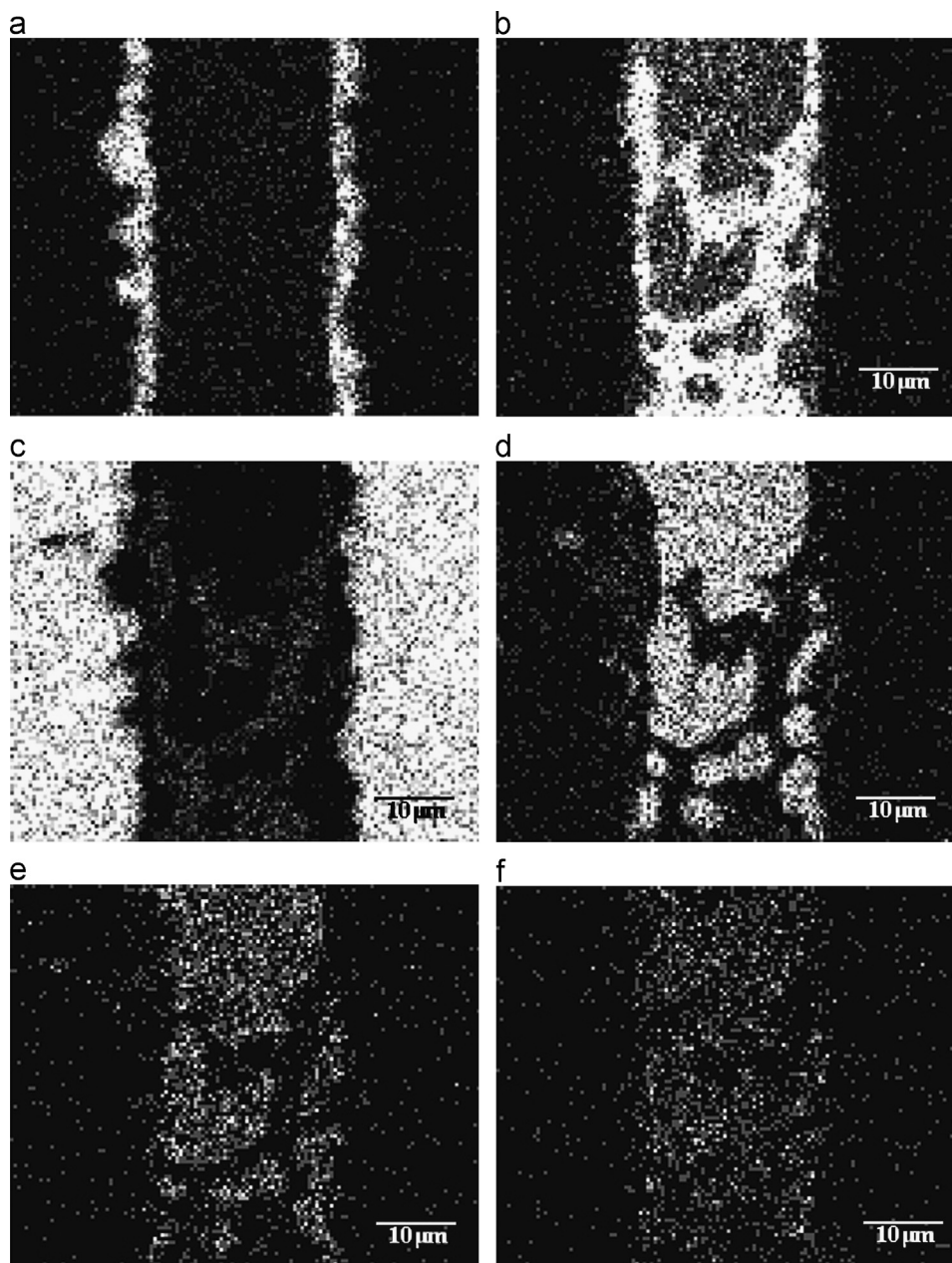


Fig. 6. Element distribution maps of V(a), Pd(b), Si(c), Au(d), Co(e), and Ni(f) for the BSEI of  $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$  joint (Fig. 5(b)).

typical ceramic fracture morphology was visible at the fractured surface of the  $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$  sample (Fig. 8(c)).

Fig. 9 presents the strength change of the  $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$  joints brazed under the optimum brazing condition with test temperature. The newly developed AuPd(Co, Ni)–V alloy filler can provide a room-temperature joint strength of 320.7 MPa, and the joints exhibit average three-point bend strengths of 221.8 MPa, 217.9 MPa, and 102.9 MPa at 973 K, 1073 K, and 1173 K respectively. As previously mentioned, though the bend strength of the  $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$  joints brazed with Au–Ni–V–Mo filler alloy is high up to 350 MPa at room temperature, the average strength values at 973 K and 1073 K are only 140 MPa and 75 MPa respectively [4]. Evidently the newly developed AuPd(Co, Ni)–V alloy filler has an advantage of

high-temperature property. According to the research results by Y. Sun et al., Au54.15–Ni36.09–Pd5–V4.76 (at%) or Au78.67–Ni15.62–Pd3.92–V1.79 (wt%) filler alloy offers a room-temperature strength of 264.4 MPa for  $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$  joints, and the joint strength at 1073 K is 214.2 MPa. When the test temperature is increased to 1173 K, it is sharply decreased to only 13 MPa [6]. This means that for the newly developed AuPd(Co, Ni)–V alloy filler both the room-temperature joint strength and the strength at 1173 K are superior to the reported Au–Ni–Pd–V filler metal.

Within the  $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$  joint brazed with Au–Ni–Pd–V filler alloy, beside the VN reaction layer at the interface, two kinds of solid solution, Au[Ni,Pd] and Ni[Si,V], were formed in the central part of the joint during the solidification process after



brazing [6]. In the present paper, the Au content in the AuPd (Co, Ni)–V alloy filler is decreased to 38.0 wt%, but the Pd content is increased to 28.0 wt %. The high concentration of Pd allows the formation of Pd<sub>2</sub>Si within the joint, and the central part of the joint is composed of AuPd(Co, Ni) alloy matrix and Pd<sub>2</sub>Si compound. According to the Pd–Si binary diagram, Pd<sub>2</sub>Si is the most refractory compound in the Pd–Si system, with a melting point of 1658 K [23]. The coarse-network-like distribution of Pd<sub>2</sub>Si within the AuPd(Co, Ni) alloy matrix throughout the joint should contribute to the stable

high-temperature strengths of the Si<sub>3</sub>N<sub>4</sub>/Si<sub>3</sub>N<sub>4</sub> joints brazed with AuPd(Co, Ni)–V alloy filler.

#### 4. Conclusions

In conclusion, a kind of AuPd(Co, Ni)–V brazing alloy with the composition of Au38.0–Pd28.0–Co18.0–Ni7.0–V9.0 (wt%) was designed as a filler for joining Si<sub>3</sub>N<sub>4</sub>. The concentration of different elements in the brazing alloy matches well with each other so that not only the filler alloy shows a suitable liquidus temperature of 1422.3 K but also the actual activity of element V for ceramic joining can be ensured. It was found

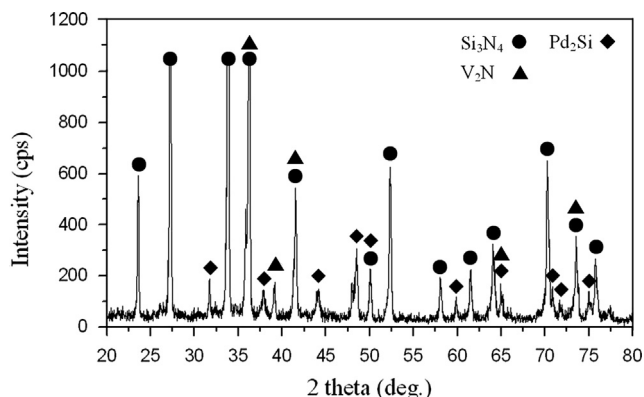


Fig. 7. X-ray diffraction pattern for the Si<sub>3</sub>N<sub>4</sub>/braze alloy interface (Brazing condition: 1443 K/10 min.).

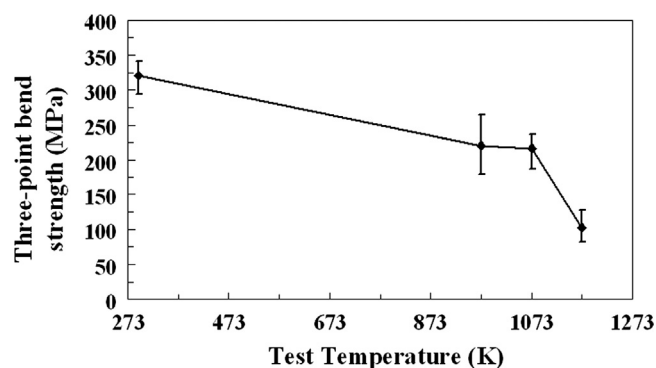


Fig. 9. Effect of test temperature on three-point bend strength of the Si<sub>3</sub>N<sub>4</sub>/Si<sub>3</sub>N<sub>4</sub> joints brazed with AuPd(Co, Ni)–V filler metal.

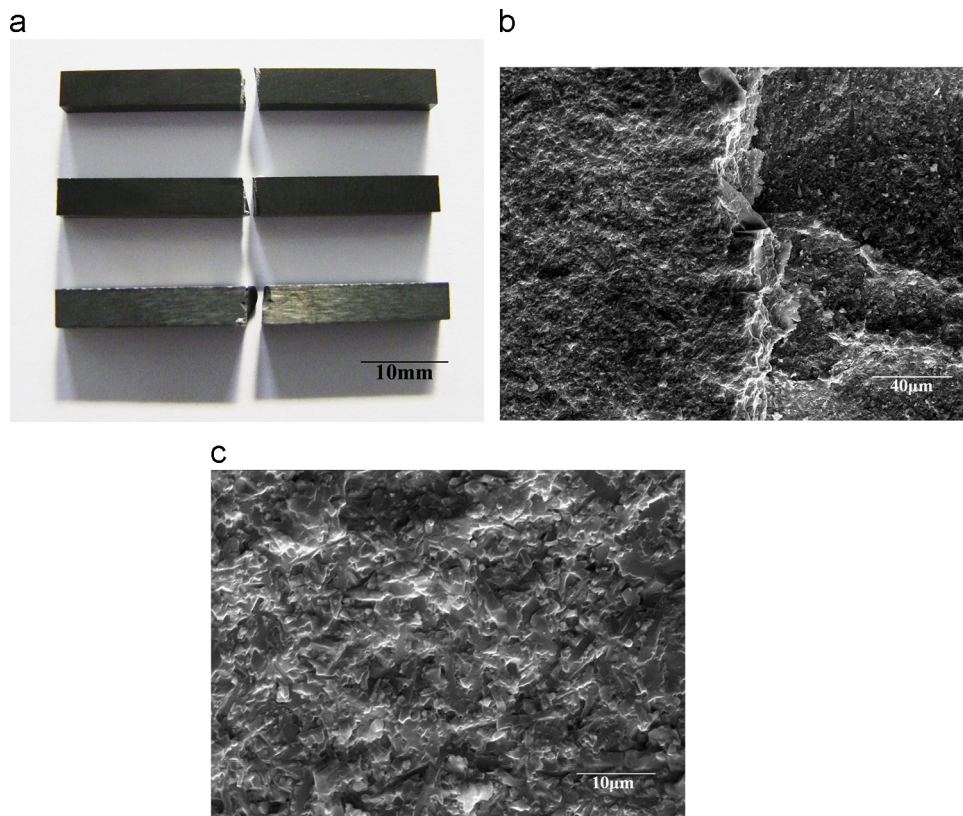


Fig. 8. The fractured Si<sub>3</sub>N<sub>4</sub>/Si<sub>3</sub>N<sub>4</sub> joint brazed at 1443 K for 10 min (a), and morphologies of fractured surface of the joint (low magnification (b) and high magnification (c)).

that, under the argon-atmosphere heating condition, the contact angle of the AuPd(Co, Ni)–V alloy on  $\text{Si}_3\text{N}_4$  was  $77.2^\circ$ .

$\text{Si}_3\text{N}_4$  ceramic has been successfully brazed to itself using the rapidly-solidified filler foils at 1443 K for 10 min. The newly developed AuPd(Co, Ni)–V alloy filler can provide three-point bend strength of 320.7 MPa for the  $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$  joints at room temperature, and the joints exhibit average bend strengths of 217.9 MPa and 102.9 MPa at 1073 K and 1173 K respectively.

The active element V with a concentration of 9.0 wt% induced the interfacial reaction and the reaction band of  $\text{V}_2\text{N}$  was formed at the  $\text{Si}_3\text{N}_4$  ceramic/filler alloy interface, with a thickness of about 3  $\mu\text{m}$ , whereas the element Pd with a concentration of 28.0 wt% allowed the formation of  $\text{Pd}_2\text{Si}$  compounds not only at the interface adjacent to the  $\text{V}_2\text{N}$  reaction bands but also within the residual brazing alloy. Furthermore, the  $\text{Pd}_2\text{Si}$  compounds exhibited a coarse-network-like distribution throughout the  $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$  joint. The elements Co and Ni did not participate in the interfacial reactions. The coarse-network-like distribution of refractory  $\text{Pd}_2\text{Si}$  compound within the AuPd(Co, Ni) alloy matrix throughout the joint should contribute to the stable high-temperature strengths of the  $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$  joints.

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