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Microstructure of brazed joints between mechanically metallized Si_3N_4 and stainless steel

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Brazing has been increasingly used to join metals to advanced ceramics. Brazing covalent materials requires either the use of active filler alloys or the previous metallization of the surface. To that end, a new and simple mechanical technique has been applied to metallize advanced ceramics, thus avoiding the use of costly Ti-based active filler alloys. The mechanical metallization of Si_3N_4 with Ti was employed as an alternative route to deposit active metallic films prior to brazing with stainless steel using 72% Ag–28% Cu or 82% Au—18% Ni eutectic alloys. The brazing temperatures were set to 40°C or 75°C above the eutectic temperature of each filler alloy. Ti-films of average thickness 4 μm produced adequate spreading of both filler alloys onto Si_3N_4 substrates, which were subsequently brazed to stainless steel. The interface of Si_3N_4/310 stainless steel basically consisted of a reaction layer, a precipitation zone and an eutectic microconstituent. Mechanically sound and vacuum-tight joints were obtained, especially upon brazing at relatively lower temperatures. Increasing the brazing temperature resulted in thermal cracking of the Si_3N_4, possibly due to increased thermal stress.

1. Introduction

Advanced ceramics such as silicon nitride have been used in an increasing number of applications including electronics, coatings, cutting tools, and especially as structural materials. Small ceramic parts are incorporated to largely metallic structures in order to reduce weight and increase operating temperatures. Structural ceramics have been able to increase aircraft payload and improve thermodynamic efficiency of turbine engines [1–6]. Brazing is by far the most widely used ceramic/metal joining process when mechanically reliable vacuum tight joints ought to be produced in large scale and are required to operate at relatively high temperatures. Superior quality directly depends on the wetting and adherence of filler alloys to the surfaces of the base materials and the brittleness of eventual interfacial reaction compounds [7–10].

Metal-ceramic brazing relies on the wettability of the ceramic surface with respect to the filler alloy. Chemically stable non-oxide ceramics, such as silicon nitride, can be either previously metallized or brazed using active filler alloys. Whereas conventional metallization methods depend on reactions with glassy intergranular phases, the addition of small contents of active metals into conventional filler alloys substantially increases their commercial value.

To improve wetting, highly stable and, therefore, inert ceramics can be metallized or brazed with active filler alloys. Metallizing Si_3N_4 employing the conventional Moly-Mn method is hard to accomplish. The microstructure of tough and commercially available Si_3N_4 suitable for structural applications contains little or no glassy intergranular phases. These are necessary to form Mn-spinels, which are the basis for the

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deposition of adherent metallic films onto ceramic surfaces [11]. Metallized surfaces can be brazed to metals using cost-effective non-active filler alloys such as Ag-Cu and Au-Ni. The addition of small amounts of Ti into conventional alloys guided the development of active alloys, which played a very important role in brazing without metallization [12–14]. Nevertheless, active Ti alloys are commercially available at prices about 10 times higher compared to non-active alloys.

Mechanical metallization of ceramics is a simple method capable of replacing both active filler alloys and chemical metallization methods. The process is based on wear of a Ti tool bit frictioned against a harder ceramic surface. Numerous advantages are associated with this process, such as: metallization occurs at room temperature; no chemicals are used and no hazardous residues are formed. The process is suitable for a large choice of coating metals or alloys and the coating area can be selected. Conventional tool machines can be easily adapted and easily automated to perform the task [15].

The major difference between active metal brazing and mechanical metallization followed by brazing is in the way that Ti is introduced. Although the ceramic surface can be coated prior to brazing, no chemical reactions take place during metallization. Moreover, Ti is dissolved in active metal filler alloys and its contents are ∼3%, whereas metallized coatings have Ti in the solid state directly in contact with the ceramic [11, 16]. From this standpoint, brazing ceramics mechanically metallized can be seen as direct brazing, since virtually all chemical reactions involving the ceramic substrate and metallic coating take place during the brazing stage. Furthermore, since metallization can be carried out in a couple of minutes as the components are being assembled, it can be considered as a simple preparation procedure, similar to filler alloy slicing and cleaning of the parts prior to brazing itself [16–18].

The development of a reaction layer and precipitation zone in brazed joints involving mechanically metallized alumina has been described elsewhere [16, 17]. The heat generated by friction during metallization is not enough to promote chemical reactions between the Ti coating and the ceramic surface. Therefore, the formation of ceramic/filler alloy/metal interfaces must have taken place during the brazing thermal cycle [16].

Similarly to what is observed in active metal brazing, it is assumed that Ti reacts with the surface of the ceramic at the brazing temperature. The formation of a metal-like compound (reaction layer) that acted as a transition layer between the ceramic and metal is mainly responsible for wetting the ceramic [16]. Ideally, the Ti film should be continuous and its thickness should not exceed a few atomic layers, enough to react with the ceramic surface and improve wetting. Ti in excess thickens the reaction layer and/or interacts with the liquid metal saturating the filler alloy and nucleating intermetallic compounds that originate the precipitation zone.

The goal of the present study was to mechanically metallize Si_3N_4 and braze it to stainless steel using 72 wt.% Ag–28 wt.% Cu or 82 wt.% Au–18 wt.% Ni alloys. The effect of wetting and brazing parameters on the microstructure of the resulting interfaces was the main aspect investigated. Further studies are still underway to determine the mechanical properties of the joints.

TABLE I Selected properties of joining materials (according to manufacturers)

Properties	Stainless steel	Si_3N_4
Product/Manufacturer	AISI 310	Ceradyne–Ceralloy 147-31N
Approximate chemical composition (wt.%)	25Cr-20Ni-1.25Mn	93% Si_3N_4
Young Modulus (GPa)	–	310
CTE (K^{-1})	–	3.1×10^{-6} (20–1000°C)
Density (g/cm^3)	7.8	3.2 (>99.5%)
K_{IC} ($MPa{\cdot}m^{1/2}$)	–	5.5–6.5

2. Experimental procedure

Si_3N_4 (Ceralloy 147–73, Ceradyne Inc., Costa Mesa, USA) pellets were mechanically metallized with Ti (DIN no. 3.7035) using previously optimized parameters (metallization time and speed) [17]. The resulting films were evaluated by optical microscopy and X-ray diffraction. Details on the metallization setup and selected parameter values can be found elsewhere [16–18].

Metallized pellets were then submitted to wetting experiments at the brazing temperatures using 72 wt% Ag–287 wt% Cu or 82 wt% Au–18 wt% Ni eutectic alloys as 0.05 mm thick foils. Prior to brazing, the base components were cleaned in an ultrasound bath of acetone. Si_3N_4 was then brazed to AISI 310 stainless steel. Their main physical and mechanical properties are summarized in Table .I

The brazing temperatures were set to 820 and 890°C for the Ag-Cu alloy (40 and 110°C above the eutectic temperature, respectively), and 990 and 1025°C for Au-Ni (40 and 75°C above the eutectic temperature, respectively). The thermal cycle consisted of two homogenization steps prior to stabilization at different brazing temperatures (Fig. 1). Brazing was carried out in a resistive furnace under high vacuum. The pressure was maintained below 3.0×10^{-5} mbar (3.0×10^{-3} Pa) throughout the entire brazing process.

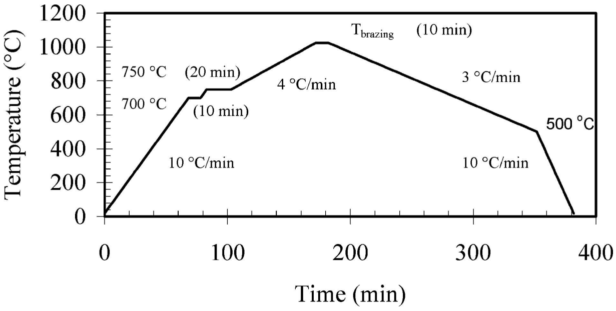


Figure 1 Brazing profile.

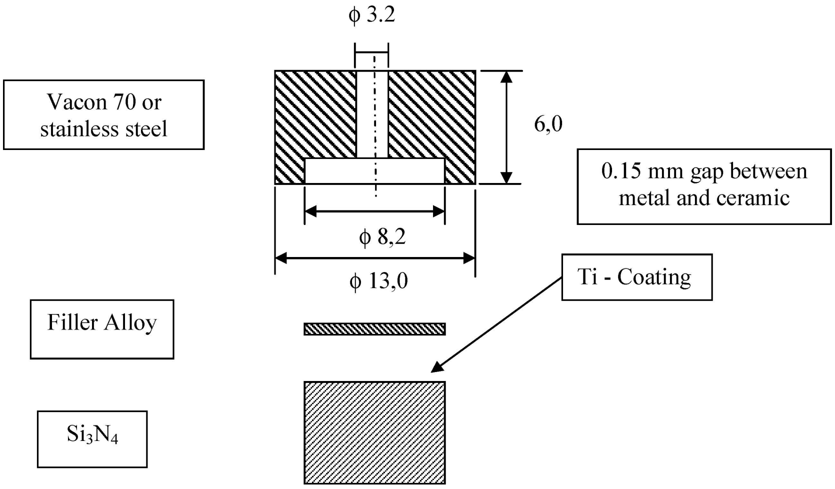


Figure 2 Schematic illustration of ceramic-metal joint design.

Joints produced using Si_3N_4 cylinders were used both for microstructural characterization and sealing tests (Fig. 2). Microstructural characterization of metal/ceramic joints took place by optical and electronic microscopy using a Reichert Jung- Polyvar microscope connected to a FC-TK – F7300U – JVC digital image acquisition system and a Philips XL-30 ESEM system, respectively. To that end, samples were sectioned using a diamond blade and mounted in cold setting polyester resin. Next, the joints were ground using SiC paper according to FEPA—P 43-GB-1984 standards (sequence 220, 320, 500, 800, 1200 mesh) and polished in diamond solution (15, 6, 3, 1 μm) and alumina slurry 0.1 μm. Finally, sealing tests were carried out using a He Leybold VL 200 leaking detector. These tests consisted in blasting He onto the outer region of joints placed under vacuum and measuring the mass of helium that penetrated the joint using a spectrometer.

3. Results and discussion

A typical metallized Si_3N_4 surface is shown in Fig. 3. The average thickness of the film was 4 ± 1 μm. Previous studies on the mechanical metallization of ceramic surfaces showed that discontinuities on the coating film were characteristic of the process. Nevertheless, the presence of defects less than 50 μm (equivalent D_{50}) did not affect wetting of the ceramic [16, 17].

Preliminary wetting tests revealed adequate spreading of the filler alloy onto Si_3N_4, substrates mechanically metallized with Ti. During brazing, Ti reacts with Si_3N_4 and molten Ag/Cu or Au/Ni. The filler alloy was activated by Ti and wetted areas not originally coated by the Ti film resulting in vacuum-tight joints. Leaking rates less than 2.0×10^{-9} mbar·L .s^{-1} were measured from Si_3N_4/stainless steel joints.

A thin reaction layer was responsible for microstructural connection between filler alloy and ceramic substrate. The reaction of Ti with Si_3N_4 produced both nitrides and silicides, as indicated in the literature [19, 20]. The Ti-Si-N phase diagram does not show the formation of ternary phases, although mixtures of binary phases are possible [19]. It should be pointed out that

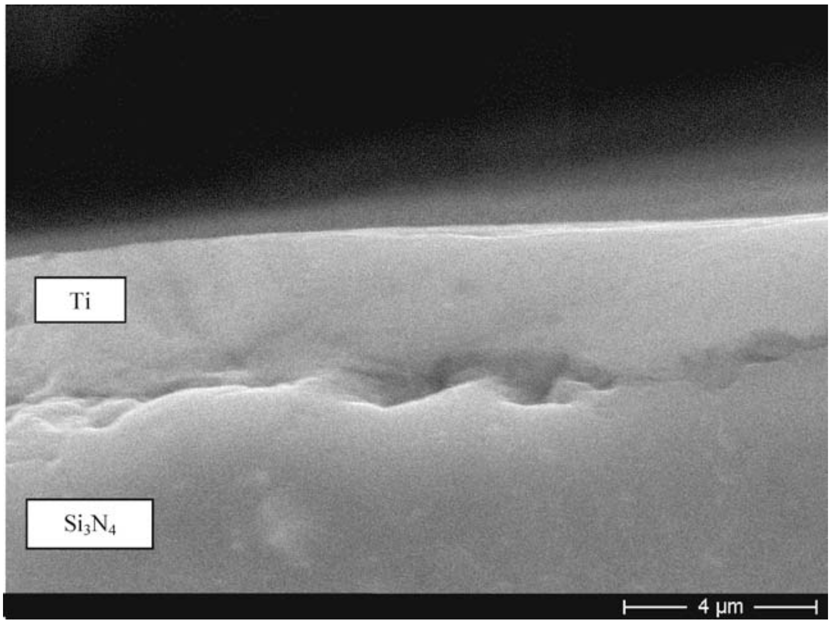


Figure 3 Cross-sectional view of Si_3N_4 metallized with Ti (SEM image).

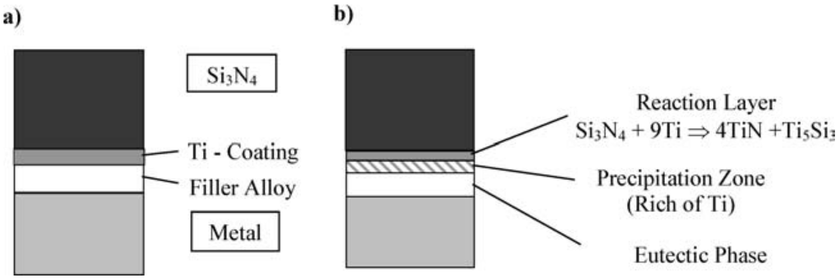


Figure 4 Schematics of interface between metal and Si_3N_4 mechanically metallized with Ti.

as Ti was not in the composition of the filler alloy, its activity, whilst in the metallic film, was equal to one.

The isothermal section at 1000°C of the ternary Ti-Si-N phase diagram shows that TiN_{1-x} is in thermodynamic equilibrium with Si_3N_4, $TiSi_2$ and Ti_5Si_3. Large amounts of nitrogen can then be dissolved [19, 20]. Therefore, at the brazing temperature, Ti can dissociate Si_3N_4 to form a compound layer consisting of titanium nitride and silicide. On the other hand, the interaction of Si and N, evolved in the dissociation of Si_3N_4, and the constituents of the filler alloy, stainless steel and Ti may also result in the formation of ternary and quaternary compounds in the Ti-rich region of the filler alloy. The presence Ti-based ternary or quaternary interfacial compounds could not be positively identified.

The mechanism of interface formation involving metallized ceramics differs from that of active filler alloys. In metallized ceramics, Ti is already in contact with the ceramic surface, whereas the use of active filler alloys requires the migration of Ti from the alloy to the ceramic. Studies on interfaces involving metallized alumina [16, 17] revealed that Ti reacted with the ceramic forming a reaction layer, but was also dissolved by the filler alloy, turning it active. The active alloy does not react with the ceramic except where Ti was not present, i.e., in areas where the Ti film was not deposited. As a result of limited reaction, a precipitation zone was formed. A schematic illustration of an interface of mechanically metallized Si_3N_4 is shown in Fig. 4. The presence of a reaction layer and precipitation zone is detailed.

The presence of a reaction layer is a necessary requirement for adequate wetting of the filler alloy on Si_3N_4. However, the negative effects of excessive growth of reaction layers should also be considered [6]. The formation of intermetallic brittle phases in the precipitation zone, as well as relatively thick reaction layers, usually reduces the overall mechanical strength of the joint. Ideally, the reaction layer should be thin and dense to allow wetting and act as a diffusion barrier to inhibit further interaction between the reactive metals of the filler alloy and the ceramic, thus limiting the formation of brittle phases [6].

The interface microstructure of Si_3N_4/310 stainless steel brazed at 820°C using the eutectic Ag-Cu filler alloy was characterized by the presence of a reaction layer, a precipitation zone and a eutectic microconstituent. A general view of the eutectic interfacial phase and base joining materials can be seen in the SEM image illustrated in Fig. 5. EDS analyses confirmed the presence of Ti in contact with Si_3N_4.

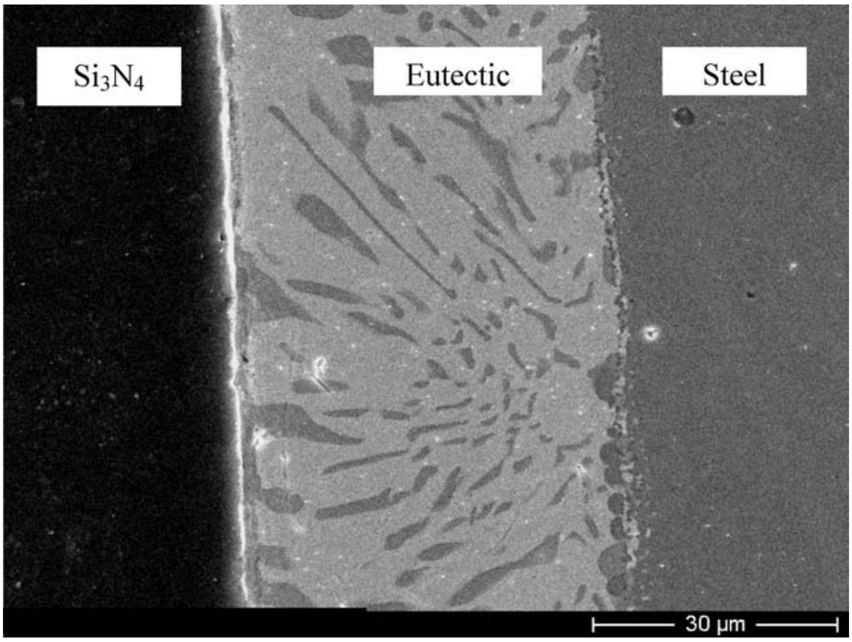


Figure 5 Interface microstructure of Si_3N_4/310 stainless steel brazed at 820°C with Ag-Cu.

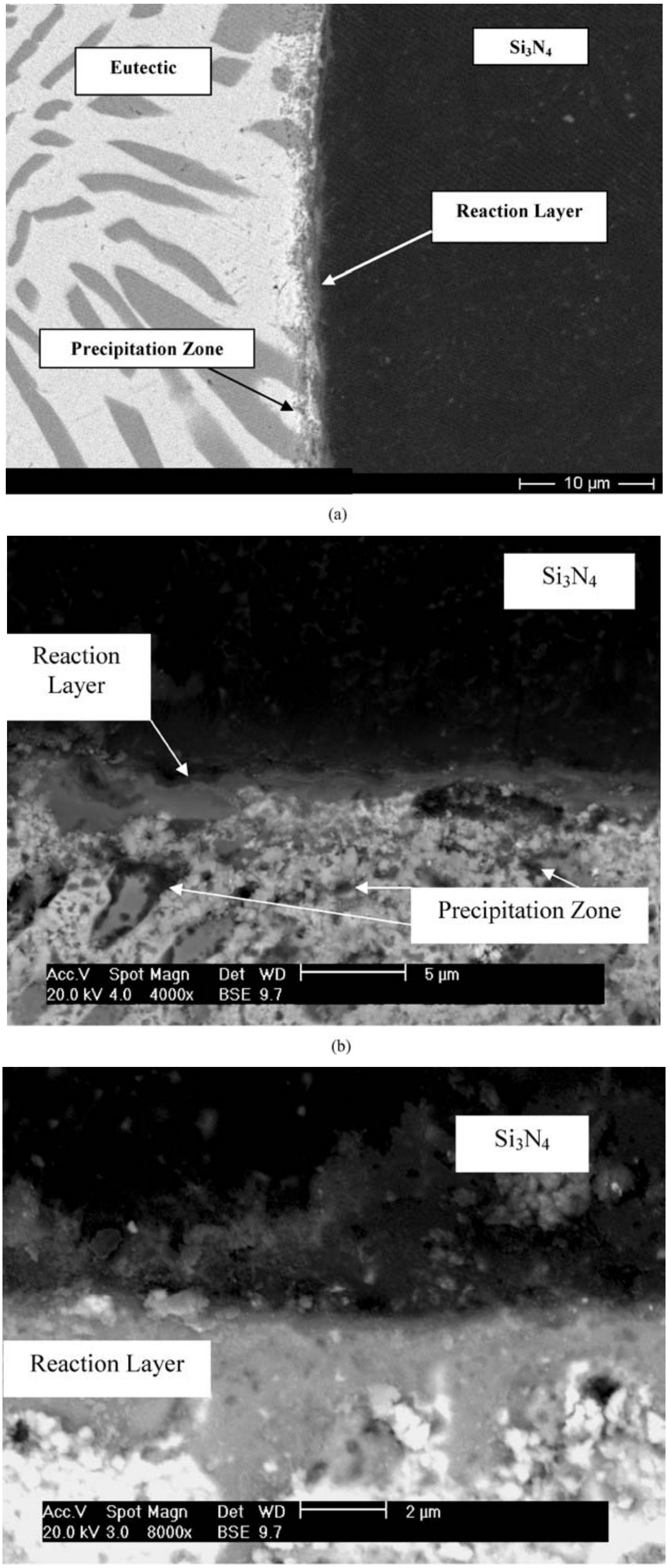


Figure 6 SEM images (BSE mode) of reaction layer and precipitation zone in joint brazed with Ag-Cu at 890°C for 10 min. (a) Overall aspect; (b) detail of the reaction layer and precipitation zone and (c) reaction layer.

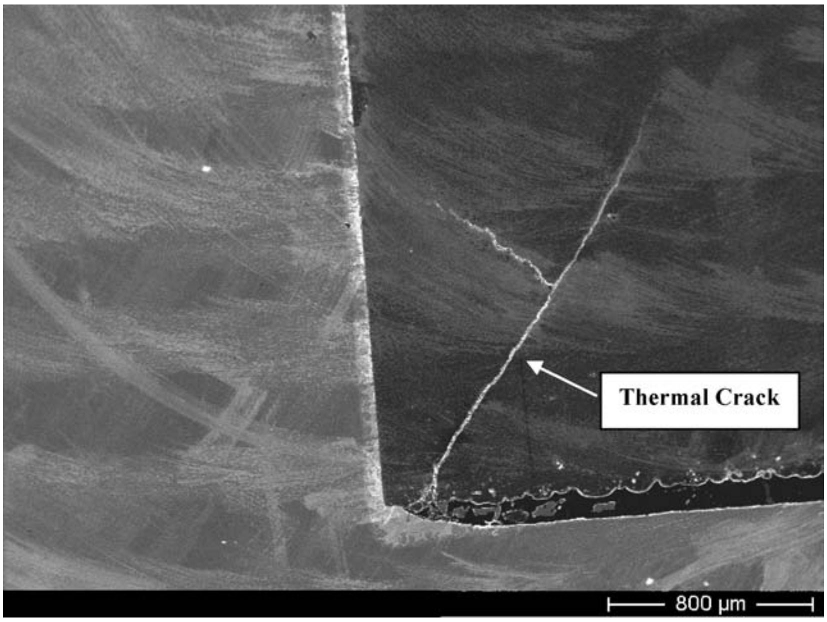


Figure 7 Thermal crack in Si_3N_4/Stainless Steel joint brazed at 1025°C using Au-Ni.

Increasing the brazing temperature to 890°C thickened both the reaction layer and the precipitation zone without significantly affecting the overall microstructural features of the interface (Fig. 6). The Ti-rich reaction layer was ~ 1 μm thick and bordered the precipitation zone. Detailed SEM and EDS analyses of the interface revealed that the reaction layer consisted basically of Si, N and Ti compounds, with the likely formation of Ti nitride and silicide, as thermodynamically estimated. The reaction layer and precipitation zone are shown in detail in Fig. 6b and c. Intermetallic compounds containing Ti and components of both stainless steel (Fe, Ni, and Cr) and Cu from the filler alloy were also detected. The presence of N in Ti could also be observed. It is not possible, however, to ascertain if the element was dissolved or reacted with Ti to form a compound.

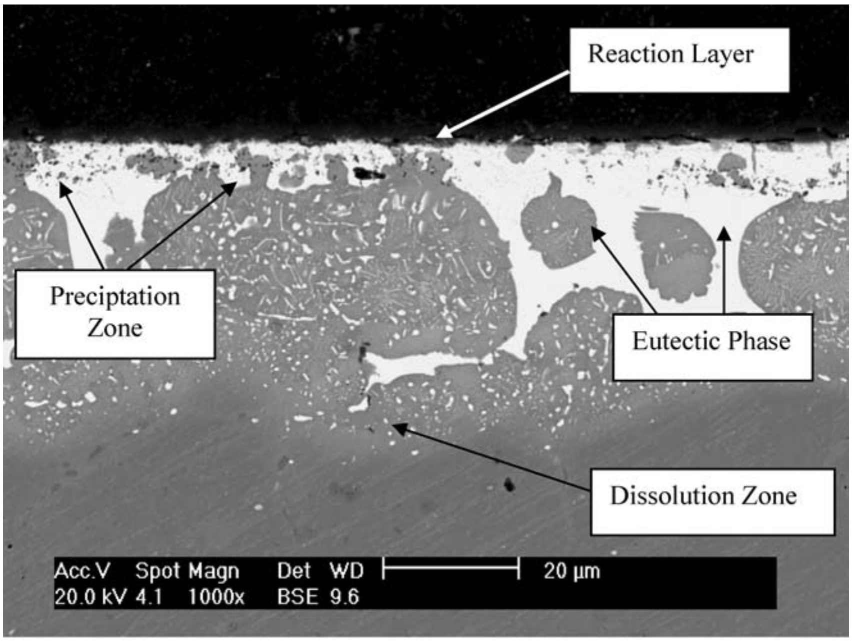
Joints brazed at 990 or 1025°C using Au-Ni were also vacuum tight. A small number of joints brazed at 1025°C depicted thermal cracks in the Si_3N_4 counterpart (Fig. 7), probably as a result of the relatively high brazing temperature responsible for mismatches in the coefficient of thermal expansion and stiffness of Si_3N_4 and stainless steel.

The microstructure of joints brazed with Au-Ni was similar to that observed in interfaces brazed with Ag-Cu, with the presence of a continuous reaction layer in the interface between Si_3N_4 and filler alloy, a Ti-rich precipitation zone and an eutectic constituent (Fig. 8a and b). The metallic component was dissolved in the filler alloy, resulting in a dissolution zone between the filler alloy and base metal.

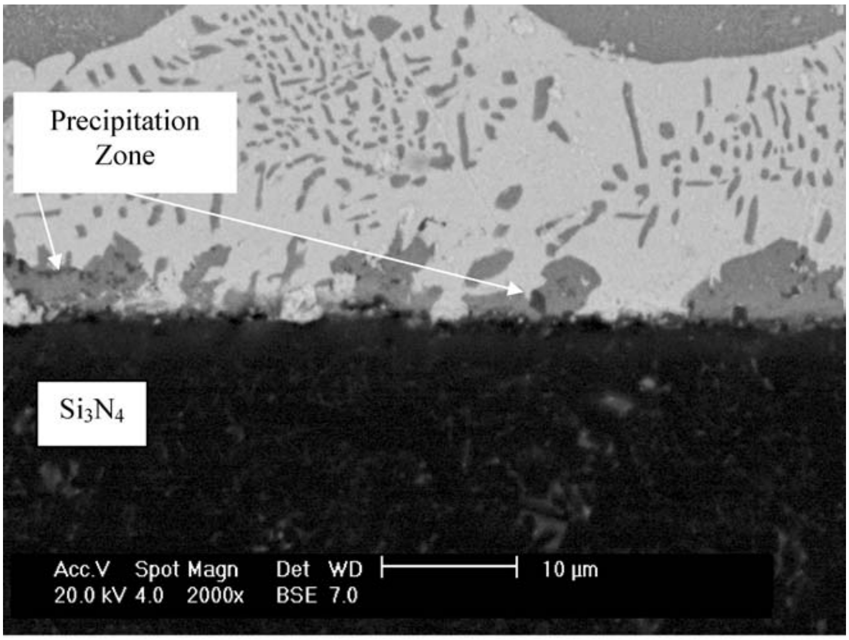
Most of the Ti deposited dissolved in the Au-Ni alloy, increasing its activity and consequently eliminating the defects originating from the mechanical metallization. Moreover, a distinct reaction layer was observed, and Ti could be detected in the other phases (precipitation zone). Such behavior was most likely attributed to the relatively high brazing temperature (990 or 1025°C), which improved the dissolution of Ti in the filler alloy and its diffusion throughout the interface. The dissolution of Ti could also have contributed to the formation of secondary phases, depending on its local concentration. EDS analyses revealed the preferential concentration of Ti in the interface with the ceramic, improving wetting. The precipitation zone mainly consisted of Ti-rich phases. The N-rich phase present in the eutectic region also contained Ti, along with Cr and Fe. The presence of these elements confirmed the dissolution of stainless steel in the molten filler alloy and the diffusion of its constituents along the area occupied by the filler alloy. Similar behavior was previously observed with other metal alloys, e.g. Vacon 70 and Kovar, joined to alumina using either active filler or mechanical metallization with Ti [16, 17]. The bright phase was rich in Au with small contents of Ti in solution, as illustrated in Fig. 8.

Finally, it should be pointed out that the stainless steel was fully wetted by the Au-Ni filler alloy despite the presence of a passivating Cr_2O_3 layer, which usually imposes an additional obstacle to brazing with conventional active-metal-free filler alloys. This result suggested that mechanically deposited Ti was dissolved in the filler alloy and reacted with the surface of stainless steel, assisting brazing and yielding a defect-free interface.

Results from microstructural analyses of Si_3N_4/stainless steel interfaces revealed that the mechanical metallization with Ti was successfully applied to Si_3N_4 regardless of the fact that the nature of the chemical reactions were different than those observed for alumina. However, due to higher CTE mismatch compared to alumina/steel couples, relatively high brazing temperatures eventually resulted in thermal cracking. Further studies on the evaluation of joint strength and the relationship with interface microstructure and stress maps are currently under way.



(a)



(b)

Figure 8 (a) Interface of Si_3N_4/stainless steel joint brazed at 1025°C using Au-Ni; (b) Precipitation zone.

4. Conclusions

1. Si_3N_4 surfaces mechanically metallized with Ti were successfully joined to stainless steel using commercially available non-active filler alloys. The resulting joints were vacuum tight. The leaking rates were below 2.0×10^{-9} mbar·L·s^{-1}.

2. Ag-28Cu and Au-18 Ni filler alloys were successfully used to join metallized Si_3N_4 to stainless steel. Increasing the temperature from 820 to 890°C did not result in significant microstructural changes on joints produced using Ag-Cu. On the other hand, brazing with Au-Ni should be carried out at 990°C to avoid substantial formation of deleterious phases and, consequently, high residual stresses.

3. Brazing at 1025°C using Au-Ni filler alloy resulted in thermal cracking due to extensive CTE mismatch associated with the relatively high brazing temperature. All other brazing conditions tested resulted in mechanically sound joints, with no evidence of thermal cracking.

4. The Ti films mechanically deposited onto Si_3N_4 surfaces reacted with the filler alloys, improving their activity and wetting both the ceramic and stainless steel.

5. The microstructure of the joints is characterized by a reaction layer and a Ti-rich precipitation zone. The stainless steel was partially dissolved by the filler alloy forming interfacial Cr, Ni, Fe and Ti-based compounds.

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