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Brazing Al_2O_3 to sintered Fe-Ni-Co alloys

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Active metal brazing has been widely used to join ceramics to metals, as sound joints are usually achieved in a single step process without special equipment. However, residual stresses may be a potential problem especially upon joining ceramics to alloys with relatively high thermal expansion coefficients. This work investigates the brazing behavior of Alumina (Al_2O_3) to a sintered Fe-Ni-Co alloy, specially designed to match its coefficient of thermal expansion to that of the ceramic counterpart. The results indicate the presence of an interfacial zone whose microstructure depends on the filler alloy employed. A relationship was established between the microstructure of the interface and the flexural strength of the joints. © *1999 Kluwer Academic Publishers*

1. Introduction

Ceramic-metal brazing has made it possible to manufacture joint components for a number of applications where ductility and toughness of metals have to be combined with the chemical and thermal stability of ceramics. Nevertheless, it has been quite well established [1–4] that thermal expansion and elastic modulus mismatches can severely compromise the final mechanical performance of the brazed components. A myriad of possible solutions has been proposed to overcome that difficulty, including graded and refractory metal interlayers [5, 6]. However, many of them are either expensive or difficult to accomplish. A simple and cost-efficient solution consists in sintering a metal alloy to have a thermal expansion coefficient as close as possible to that of the ceramic counterpart. Casted Fe-Ni and Fe-Ni-Co alloys with low thermal expansion coefficients have been produced for a long time. Nevertheless, the presence of small amounts of impurities such as C, Si, and Mn affect their overall expansion behavior [7]. In addition, stamping or machining are often required to produce the final shape of a component, thus increasing costs [8]. Powder metallurgy has been proven to be an efficient approach to produce near-net shape components of low-expansion alloys, particularly useful on Al_2O_3-metal joints [9]. Within a reasonable degree of accuracy, the composition of the alloy and sintering parameters can be adjusted to result in a coefficient of thermal expansion that matches that of the Al_2O_3. In addition, the contents of impurities are drastically reduced, which contributes to a more efficient microstructural design.

The sintered component can then be used as either an interlayer or as the metal counterpart itself. The presence of a metallic interlayer not only limits the development of thermal residual stresses but also may act as a plastic buffer, accommodating excess stresses. Casted Fe-Ni-Co alloys, such as Kovar, have been broadly used as the metallic substrate of joints with alumina in the manufacture of high-vacuum seals and electronic devices, in addition to structural components [10, 11]. Nevertheless, whereas the low expansion behavior of kovar is typically constrained to a narrow temperature range, sintered Fe-Ni-Co alloys may depict a similar behavior in adjustable, and frequently wider, temperature ranges [9].

Active brazing alloys are typically characterized by relatively high thermal expansion coefficients. However, their role upon joining is to react with the ceramic substrate, quite often resulting in oxide layers, whose thermal expansion should not depart considerably from that of the ceramic substrate. In addition, the reaction layers are usually thin enough, so that it should be quite straightforward to assume that their presence does not contribute significantly to the final stress distribution of the joined component.

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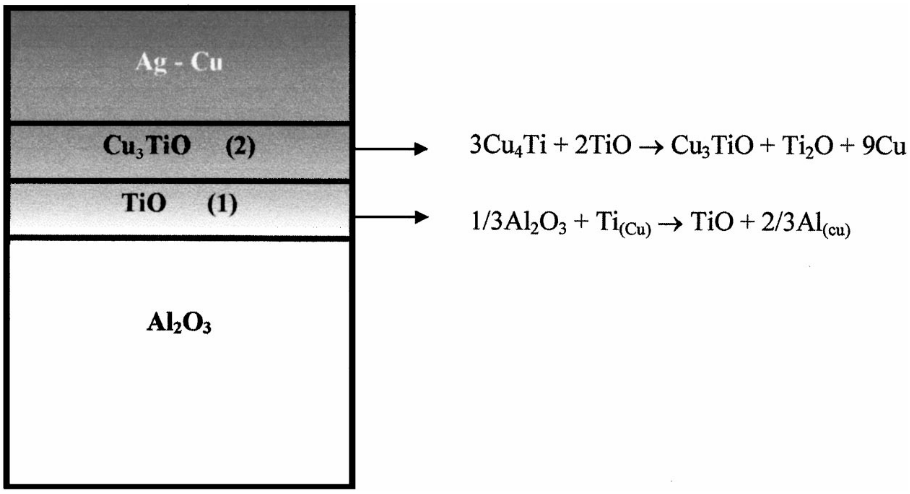

Figure 1 Schematic representation of phases present in the reaction layer.

The objective of the present work was to study the influence of brazing parameters in the microstructure of the interface and flexural strength of Al_2O_3/sintered Fe-28wt %Ni-18 wt %Co joints. Two different active filler alloys have been addressed, i.e., Incusil ABA (Ag-27.25wt %Cu-12.50wt %In-1.25%wt Ti) and Ticusil (Ag-26.70wt %Cu-4.50wt %Ti).

2. Al_2O_3/Metal active brazing

The role of titanium in active filler alloys is to dissociate the surface of Al_2O_3, thus improving its wettability. Although Al_2O_3 is thermodynamically more stable than the resulting Ti-oxide film, the reaction to form the latter due to the difference in free energy of the surface compared to the bulk, i.e.: [12]:

$$\Delta G \mathrm{Al_2O_3^{Surf.}} > \Delta G \mathrm{Al_2O_3^0} \qquad (1)$$

where $\Delta G \mathrm{Al_2O_3^{Surf}}$ and $\Delta G \mathrm{Al_2O_3^0}$ are free energy of surface (Al_2O_3) and standard free energy (Al_2O_3), respectively.

The reaction between the surface of Al_2O_3 and the molten filler alloy assures the required wetting, according to the following general equation [12, 13]:

$$\mathrm{Al_2O_3^{surf.}} + 3x\mathrm{M} \Leftrightarrow 3\mathrm{M}_x\mathrm{O} + 2\mathrm{Al} \qquad (2)$$

where M represents the filler alloy active metal. The growth of the interfacial reaction layer improves wetting as a consequence of the free energy resulted from the formation of a new phase, thus improving the adherence of the metal-Al_2O_3 interface. On the other hand, interfacial compounds are generally brittle and thick layers often have a deleterious effect on the performance of the joint [14].

Ti and Al_2O_3 react together to form a thin layer of Ti-oxides, such as TiO, Ti_2O_3, Ti_3O_5, Ti_4O_7, and TiO_2, whose stoichiometry depends on the activity of the Ti in the filler alloy [6, 13, 15, 16]. A second layer usually forms on top of the primary Ti-oxide layer, as a result of the reaction between Ti and Cu in the filler alloy. The product of such a reaction usually involves a ternary Cu-Ti-O compound [17, 18]. Thermodynamic and kinetic aspects of Al_2O_3-filler alloy interfaces have been extensively studied in an attempt to better understand the mechanisms of interface evolution [16–19]. Fig. 1 shows the distribution of phases along with the corresponding chemical equations proposed by Suenaga and Chindabaram to explain the microstructure of the reaction layer [17, 18]. In that set of equations, $Al_{(Cu)}$, originating from the reduction of Al_2O_3, and $Ti_{(Cu)}$, which plays a role in such reduction reaction are both dissolved in the Cu present in the filler alloy [17, 18].

At the brazing temperature, Ti coming from the filler alloy diffuses onto the surface of Al_2O_3 and drives the dissociation of the ceramic into aluminum and oxygen. Aluminum initially forms a solid solution with copper and it is later dissolved by the previously formed Cu-Ti-O compound [17, 18]. Oxygen reacts with titanium, according to Equation 2, resulting in the primary Ti-oxide layer which coats the entire surface of the ceramic [17]. Other sources of oxygen may be originated from the filler alloy itself, which can contain either oxides or dissolved oxygen, and the brazing atmosphere, since the pressure employed (1.0×10^{-5} mbar) is well above the O_2 equilibrium pressure required to prevent the oxidation of Ti, i.e., 1.0×10^{-19} mbar [4].

3. Experimental

3.1. Sintering Fe-Ni-Co alloys

Powdered Fe-28 %Ni-18 %Co (in wt %) alloys were sintered from elemental powders whose characteristics are given in Table I. The powders were mixed in a Y-mixer for 80 min adding 0.7 wt % lubricant (zinc stearate). Cylindrical samples of 9.5 mm in diameter and 10.0 mm high were then uniaxially pressed using a double action pressing with a moving die body. Sintering was carried out at 1240 °C for 120 min followed by furnace cooling (15 °C/min). The sintering cycle included a soaking period of 30 min at 450 °C to remove the lubricant. Further details on the production of powdered Fe-Ni-Co alloys can be found elsewhere [9].

In order to rule out any effect of the pores on the coefficient of thermal expansion of the alloys, the samples

TABLE I Characteristics of the starting powders

	Fe	Ni	Co
Specification	Ancorsteel 1000B	Carbonila type 123	EF-atomized
Si (wt %)	<0.01	—	—
S (wt %)	0.009	0.0001	—
C (wt %)	<0.01	0.063	—
O (wt %)	0.09	0.09	—
P (wt %)	0.005	—	—
Mn (wt %)	0.10	—	—
Co (wt %)	—	—	99.99
$D_{average}$ (μm)	94	4.1	10

were sintered to achieve 90% of their theoretical density [20]. It has also been showed that, at that level of porosity, no infiltration is expected to take place for the filler alloys used [21].

3.2. Brazing Fe-Ni-Co/Al_2O_3

A sequence of joints were produced varying the brazing temperature and time, as well as the filler alloy according to conditions shown in Table II.

The ceramic surfaces to be brazed were ground with a 220 mesh sand paper, whereas the metallic ones were ground with a 600 mesh sand paper. Ceramic/metal couples were then mounted using a layer of filler alloy 0.1 mm-thick and held together in the furnace under an applied load of 11.07 kPa. Brazing was carried out under vacuum of 3.0×10^{-5} mbar. Initially, the samples were heated up to a temperature 25 °C below the *solidus* temperature of the filler alloy for a soaking period of 30 min. This step aimed to achieve the thermal equilibrium of the couple, since there is a reasonable difference in the thermal conductivity of the materials, i.e., 30 W/m · K for Al_2O_3, and about 80 W/m · K for Fe-Ni alloys. The sample was then heated up to the brazing temperature (Fig. 2).

TABLE II Brazing experimental conditions

Time (min)	720 °C (Incusil)	750 °C (Incusil)	855 °C (Ticusil)	885 °C (Ticusil)
15	A1	C1	B1	D1
30	A2	C2	B2	D2

Incusil and Ticusil are filler alloys.

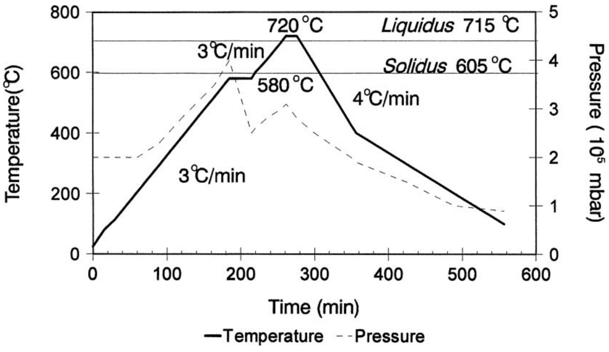

Figure 2 Brazing temperature and pressure profile.

3.3. Characterization

The brazed joints were characterized as for the microstructure of their interface and mechanical strength of the couple. The microstructural characterization was by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) using a Philips XL-30 microscope. Three-point flexural strength tests were then carried out using a universal MTS-810 test equipment whose actuator was set to a speed of 0.1 mm/min.

The final mechanical properties of the joint can be drastically affected by the precipitation of interfacial oxide layers, which in some cases can limit the joint strength [14], since such compounds are usually brittle. In addition, ceramics are quite susceptible to the presence of cracks and flaws which can subcritically grow at the service stress levels, leading to the joint catastrophic failure [22–24].

4. Results and discussion

4.1. Microstructure

SEM imaging of interfaces brazed according to profile A (cf. Table II) revealed the presence of three distinct phases. Fig. 3 illustrates such an interface and the phases are labeled as 1, 2 and 3N. Phase 1 is distributed throughout the interface and its average composition, as estimated by EDS analysis, is 84%Ag-11%In-5%Cu. Copper is the dominant element in phase 2, which contains also approximately 9% Ag. This compound is seen dispersed in phase 1. Finally, a minor phase (3N) with composition 30%Cu-26%Ti-9%Ag can be observed dispersed preferentially in small areas in the vicinity of the metallic substrate. By increasing the brazing time from 15 to 30 min (condition A1 to A2), a compositional change of phase 3N is observed by the incorporation of small amounts of Fe and Co. In addition to interfacial compounds, small pores (2–3 μm) were also observed distributed preferentially in phase 1, along with an indication of little infiltration of the filler alloy into the open pores of the metallic compound. Nevertheless, at this level of total porosity (10%), it has been demonstrated that the infiltration of small amounts of the filler alloy does not compromise the reliability of the joint [21].

The ternary Ag-Cu-In phase diagram [25] indicates the precipitation of phase 1 under equilibrium conditions. Such a compound consists of a solid solution with small Cu precipitates. Phase 2 is also likely to be a Ag-Cu solution rich in the latter, as suggested by the corresponding binary equilibrium [26]. An analysis of the Cu-Ti and Ti-Ni [26] equilibrium diagrams suggests low solubilities of those elements, as well as the presence of several intermetallic compounds. As Cu-Ni consists of an isomorphous system, it could be inferred that phase 3N consists of a Ti-Ni-Cu intermetallic compound. In addition, a careful examination of the equilibrium diagram isothermals of the brazing temperature indicated that phase 3N could, in fact, be formed upon cooling of the molten filler alloy where Ni has been dissolved. It should also be pointed out that no mixed Ti-Cu-Al oxide layer could be observed, which indicated that Ti from the filler alloy was entirely

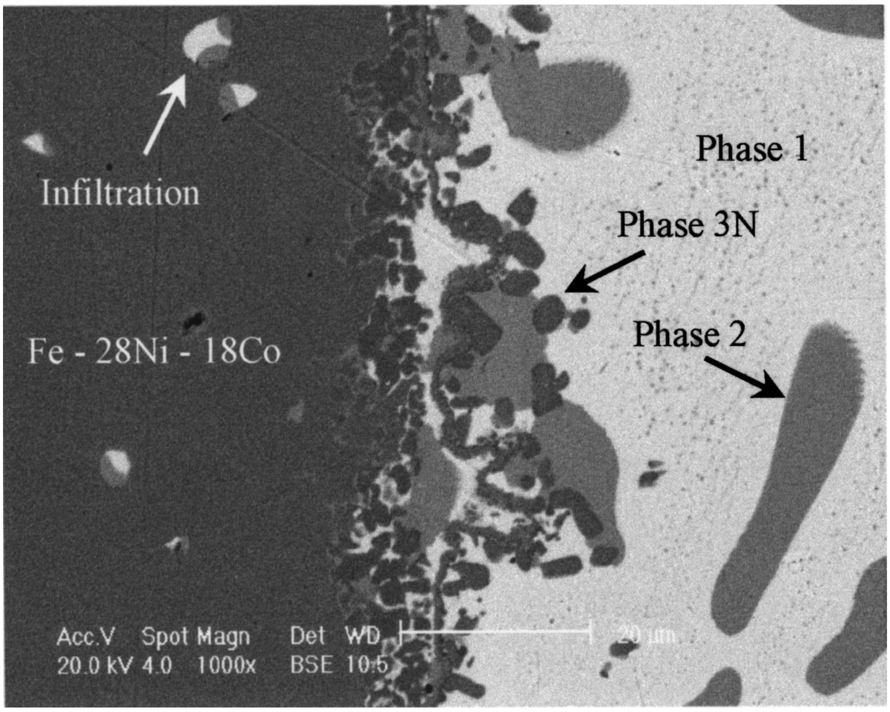

Figure 3 Microstructure of joint brazed with Incusil ABA at 720 °C for 30 min.

consumed in the formation of phase 3N, which is probably more stable than any of the oxides that might have formed.

Increasing the brazing temperature from 720 to 750 °C did not result in any substantial change in the microstructure of joints brazed with Incusil ABA. As it should be expected, both Fe and Co contents of phase 3N were around 2%. However brazing with Incusil ABA wetted the surface of Al_2O_3, which is consistent with the establishment of sound and relatively flawless interfaces, no reaction layer could be noticed under any of the brazing conditions carried out. Although it is possible that a extremely thin reaction layer might have been formed and could not be detected due to experimental limitations, it is also likely to assume that wetting occurred as a consequence of In in solution with Ag in phase 1.

On the other hand, brazing with Ticusil resulted in the precipitation of a reaction layer under all conditions investigated. Little infiltration of the molten filler alloy into the open pores of the Fe-Ni-Co alloy could also be seen. The interface of joints brazed according to condition B1 (855 °C/15 min) included five distinct phases, one of them being a reaction layer containing high Ti contents (36%), in addition to Cu (17%), Fe (15%), Ni (13%), Ag (10%), and traces of Co, Al, and O. The phase 1 is distributed throughout the interface and its average composition is 96%Ag-4%Cu. The phases 2, 3N e 4F are preferentially distributed in the central zone of the interface, as it can be seen from Fig. 4.

The composition of phase 2 consists of 76%Cu-12%Ag-4%Ni in addition to traces of Fe, Ti, Co, and O. This phase can be seen dispersed in the matrix (phase 1). Phase 3N revealed an average composition 48%Ni-20%Ti-10%Fe-9%Cu-8%Co and traces of Ag and O. Finally, a Fe-rich phase (4F) of average composition 48%Fe-25%Ti-11%Ni-8%Co-bal.Ag-Cu-O was also noticed dispersed in phase 1 (Fig. 5). The presence of phase 3N and its coexistence with phase 4F have not yet been explained. Traces of Fe, Ni, and Co have also been detected in virtually all new formed phases, included the reaction layer. The presence of the phase 4F has been reported in ceramic-metal joints brazed using Cusil as the filler alloy, where the ceramic substrate was previously activated TiH_2 [27]. By increasing the brazing temperature and time the composition of the phases formed from condition B1 (855 °C/15 min) did not change considerably. Nevertheless, as the brazing time increased from 15 to 30 min, phase 4F spread out.

The presence of traces of Fe, Ni, and Co in all compounds precipitated in interfaces brazed with Ticusil can be rationalized in terms of the brazing temperature. Diffusion of the metallic components into the molten filler alloy was enhanced by the relatively high brazing temperature, as compared to that employed to braze with Incusil ABA. In addition the precipitation of phase 4F is likely to take place as a consequence of the high solubility of Fe in the molten Ti-Cu alloy. As the temperature decreased and the alloy gradually solidified, a supersaturated solid solution may have formed and led to the precipitation of phase 4F.

In summary, Fe-Ni-Co/Al_2O_3 joints brazed with Incusil did not show the presence of an interfacial reaction layer. In addition, the presence of a Ni-rich phase in the central brazed zone may also be deleterious to the mechanical strength of the interface, due to its inherent brittle behavior. The same argument applies to the presence of phases 3N and 4F in interfaces brazed with Ticusil. Nevertheless, in this case, the precipitation of a reaction zone throughout the interface may counteract that effect.

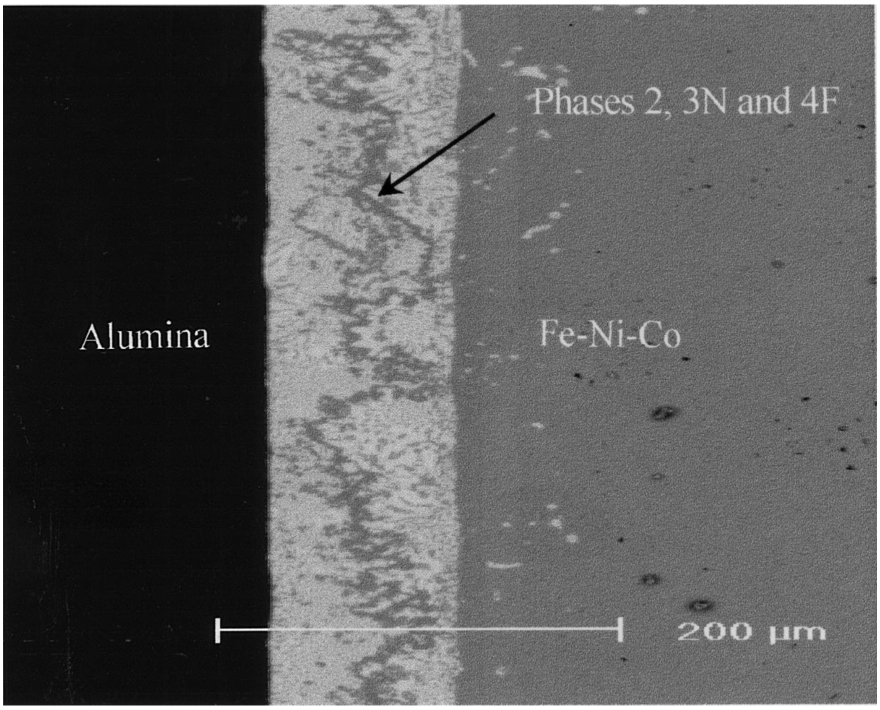

Figure 4 Microstructure of joint brazed with Ticusil at 855 °C for 15 min.

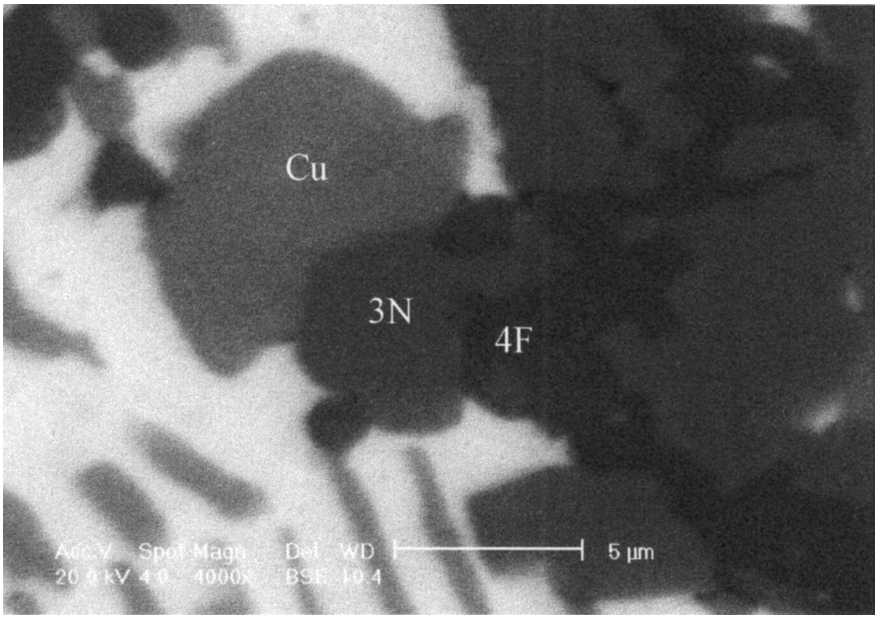

Figure 5 Detail of the microstructure of joint brazed with Ticusil at 885 °C for 15 min.

4.2. Mechanical strength

The mechanical strength of Fe-Ni-Co/Al_2O_3 joints was evaluated by 3-point flexural tests. The results revealed a significant scatter in strength, as shown in Table III for joints brazed with Incusil. This behavior can be attributed to the concentration of thermal-residual stresses at and near the interface. Regardless of the relatively large error bars, it was possible to establish trends between the mechanical strength data and the microstructure of the corresponding interfaces.

TABLE III Mechanical strength of Fe-Ni-Co/Al_2O_3 joints brazed with Incusil ABA

	720 °C		750 °C	
	15 min	30 min	15 min	30 min
Strength (MPa)	110	121	118	115
Standard deviation (MPa)	50	27	52	50

Joints brazed with Incusil ABA show similar average strengths, regardless of the brazing parameters. This is related to the fact that beside the relative concentration of phases, the microstructures of the resulting interfaces were not substantially affected by changes in brazing temperature and time. The absence of a reaction layer resulted in relative low strength average values. The scatter in strength values apparently increased for joints brazed under conditions C1 and C2. That can

TABLE IV Mechanical strength of Fe-Ni-Co/Al_2O_3 joints brazed with Ticusil

	855 °C		855 °C	
	15 min	30 min	15 min	30 min
Strength (MPa)	107	102	131	123
Standard deviation (MPa)	33	38	47	45

be attributed to the precipitation of phase 3N (48%Ni-20%Ti-10%Fe-9%Cu-8%Co—traces of Ag-O), which may have enhanced the development of peak stress areas.

Joints brazed with Ticusil developed a reaction layer in addition to phases 3N - rich in Ni, and 4F - rich in Fe, in all investigated brazing conditions. The presence of a reaction layer in joints brazed under conditions B1 and B2 may have improved the mechanical strength of the interface, nevertheless such an effect was probably counteracted by the deleterious presence of brittle phases rich in Ni-Ti (3N), and Fe-Ti (4F) dispersed in the microstructure. Increasing the brazing temperature from 855 to 885 °C enhanced the mechanical strength of the joints. Table IV shows that the average mechanical strength of joints brazed with Ticusil reached a maximum of 131 MPa for brazing condition D1 (885 °C/15 min). Such an interface revealed the presence of an uniform reaction layer responsible for establishing a chemical bridge between the base materials. The effect of increasing the time to 30 min was masked by the large error bars inherent to the tests, nevertheless a decrease in the average strength value can be expected as a response of the system to the growth of phases 3N and 4F, concentrated preferentially in the central brazed zone.

The presence of ceramic and metallic particles on the fracture surface of Fe-Ni-Co/Al_2O_3 joints following the strength tests indicated that fracture occurred in a brittle fashion. The crack path was a twisted one and ran preferentially through the ceramic and phases 3N and 4F, confirming the brittle nature of those compounds.

In summary, joints brazed with Incusil ABA revealed an inferior mechanical behavior as compared to those brazed with Ticusil. This behavior was associated with the absence of an interfacial reaction layer and the precipitation of brittle phases (3N). Although the development of a reaction zone in the latter case initially improved the mechanical strength by establishing a chemical bridge between the substrates, its excessive growth along with the precipitation of brittle phases were deleterious to the joint. The mechanical strength values obtained in the present work are comparable to those for similar joints that used conventional Fe-Ni-Co alloys [4, 28, 29].

5. Conclusions

1. Fe-Ni-Co/Al_2O_3 joints brazed by using Incusil ABA as the filler alloy did not result in the formation of interfacial reaction layers. On the other hand, joints brazed with Ticusil showed a reaction layer for all investigated brazing conditions.

2. Brazing with Incusil ABA leads to Ni-Ti rich areas located preferentially along the central region of the interface. This phase probably resulted from the dissolution of Ni from the metallic substrate into the filler alloy.

3. In addition to a Ni-Ti rich phase, joints brazed with Ticusil also showed Fe-Ti rich areas, as a consequence of the higher, required brazing temperatures, leading to a increased Fe solubility in the filler alloy and consequently in the precipitation of intermetallic phases.

4. The mechanical strength of the joints revealed significant scatter and a close relationship with the microstructure of the corresponding interfaces. Whereas the presence of phases 3N and 4F was deleterious to the mechanical strength of the joints, due to their brittle nature, the development of a reaction layer improved the average strength of joints brazed with Ticusil.

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