# Characterization and brazing of sintered Ni–Al–Co powder mixtures containing intermetallics

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# Characterization and brazing of sintered Ni-Al-Co powder mixtures containing intermetallics

**Abstract:** Powder metallurgy is a progressive branch of engineering that enables engineers to fabricate difficult-to-make parts and materials that are used in many industrial areas. Joining this class of materials is a difficult task due to their intrinsic limitations, such as porosity and thermal properties. In this study, varying ratios of Co powder additions to $Ni_x$+$Al_y$ powder mixture were made prior to sintering at 600°C. The sintered samples were brazed in both microwave and traditional tube furnaces by placing brazing filler alloy between the sintered specimens without added weight at 950°C for 15 min. Scanning electron microscopy and X-ray diffraction techniques were employed to characterize the brazed samples and the joints. Shear strength and hardness of brazed joints were also determined.

**Keywords:** brazing; intermetallics; powder; sintering.

## 1 Introduction

Powder metallurgy has given an enormous capacity to the processing of traditional metals and alloys as well as advanced materials known to researchers. This method can also be used to synthesize intermetallic phases such as FeAl, $Fe_3Al$, NiAl and $Ni_3Al$, which are a few of the advanced technological materials that have outstanding mechanical and corrosion properties for high temperature applications [1–6]. Intermetallic compounds have many advantages such as high melting points, low densities, high strength, as well as good corrosion and oxidation resistance, which make them an attractive candidate for high-temperature structural use. However, low ductility and brittleness at ambient temperature and additional processing problems seriously limit their industrial application [1, 7–9].

Alloying additions can improve the inferior properties of intermetallics, e.g., boron additions could dramatically improve the ductility of $Ni_3Al$ at ambient and high temperatures [7, 8]. Brazing, as one of the popular methods of joining in industry, can be successfully used in difficult-to-join and different groups of materials attempted by researchers by using filler metals with different properties [10, 11]. The process of brazing can be carried out in a vacuum, reactive and inert medium, and with conventional heating, microwave heating and infrared heating [12–17].

Ni alloys are extensively used in aerospace, electrical industries because of their thermal and alloying properties [18–20]. Some Ni alloys have been studied extensively for magnetic applications, especially in microsystem technology for the manufacturing of sensors, actuators, micro-relays and inductors. One of the newly developed electrical transformer materials, Co-Ni-Al alloy, exhibit a narrow thermal hysteresis (<30°C), and ferromagnetic shape memory (FSM) behavior [21, 22]. A range of compositions and heat treatments of Ni-Al-Co elements was studied in the past in an effort to understand and develop accurate phase diagrams [22–24]. It has been particularly established that Co addition provides encouraging results such as high hardness and shear strength [25]. The microwave sintering received attention because of its competitive unique characteristics, i.e., volumetric heating of samples from inside out and containing lower thermal gradient effects compared to traditional sintering methods [17, 26] and its lower sintering temperatures with higher heating rate allows the short processing time with lower energy consumption; highly improved mechanical properties from microwave sintered specimens were also realized [27–29].

The purpose of this study was to braze Ni-Al-Co powder mixtures sintered in microwave and traditional tube furnaces at 950°C for 15 min. Two different brazing alloys with and without Ag were selected for the joining of Ni-Al-Co powder mixtures.

## 2 Experimental method

Starting powders employed in this study were as follows: the purity of 99.8% for Ni powders with a particle size

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lower than 40 µm, the purity of 99.95% for Al powders a particle size lower than 75 µm and the purity of 99.9% for Co powders with a particle size lower than 150 µm. The composition calculated according to formula $Ni_{x+}Al_y+Co_{100-(x+y)}$ (x+y=97, 94, 90, 85 in at %), that is, 3 at % Co, 6 at % Co, 10 at % Co, and 15 at % Co specimens were prepared in 11 g rectangular compressed pre-form. They were mixed homogenously for 24 h in a mixer following the weighing. The mixture was shaped by single axis cold hydraulic pressing using high strength steel die. A pressure of 300 bar was used for compacting all the powder mixtures. The cold pressed samples underwent a sintering at 600°C for 2 h in a traditional tube furnace using Argon gas atmosphere. The brazing process was carried out in both microwave and traditional tube furnace at 950°C for 15 min and 1000°C for 15 min, respectively. The specimens were cooled in the furnace after sintering and their hardness and shear strengths measurements were carried out using METTEST-HT (Brinell) hardness tester (Germany), and Shimadzu Autograph AG-IS 100KN (Shimadzu, Kyoto, Japan) universal tensile tester machine, respectively. S2 and S28 brazing alloys, of which their compositions are given in Table 1, were chosen to join the specimens. Two sets of brazing alloys were chosen, i.e., S2 without Ag and S28 with Ag. After the brazing process, standard metallurgical specimen preparation was made to reveal the microstructure of the joints and powder compacts.

Shimadzu XRD-6000 X-Ray Diffraction analyzer (Shimadzu, Kyoto, Japan) was operated with Cu K alpha radiation at the scanning rate of 2 degree per minute. LEO 1430 VP model Scanning Electron Microscope (Carl Zeiss-Leica Ltd., Jena, Germany) fitted with an Oxford EDX analyzer (Oxford Instruments, Abingdon, Oxfordshire, UK) was used for microstructural and EDX compositional analysis.

The volumetric changes of Ni+Al+Co composite material after sintering were calculated by using the (d=m/V) formula (Figure 1). The volume of pre-sintered and post-sintered samples was measured by the Archimedes principle. All the percentages and ratios are given in weight percent unless stated otherwise.

**Table 1** Compositions of S2 and S28 brazing alloys used in this research (in wt%).

| Alloys | Cu | Sn | Si | Ag | Zn |
|---|---|---|---|---|---|
| S2 | 59 | 1.8 | 0.2 | – | Bal. |
| S28 | 60 | – | 0.2 | 2 | Bal. |

# 3 Results and discussion

## 3.1 Structural analysis

After sintering, X-Ray Diffraction (XRD) analysis was performed on the samples. The XRD graphics of Ni+Al+3% Co composite material and Ni+Al+15% Co composite are given in Figures 2 and 3, respectively. It was shown that Ni, Co and Al reacted to yield metal matrix Ni composite with $Ni_3AlCo$, Ni and NiAl phases.

The XRD analysis result of 15% Co added mixture can be seen in Figure 3. As shown in the figure, the $(Ni,Co)_3Al$ intermetallic phase has formed in addition to stoichiometric NiAl intermetallic phase. Ni (γ) phase has the highest peak value. The Ni element may be the most freely distributed highest constituent within the composite material. It can also be deduced that Al and Co have been combined to produce intermetallics or the remaining Al or Co is below the detection limit of the XRD analyzer.

It can be deduced from Figures 2 and 3 that all the phases formed in the Ni+Al+Co mixture after sintering are $(Ni, Co)_3Al$, NiAl, Ni(γ). NiAl and (Ni, Co)3Al phases are the ordered intermetallics of Ni, Co and Al. The amount of

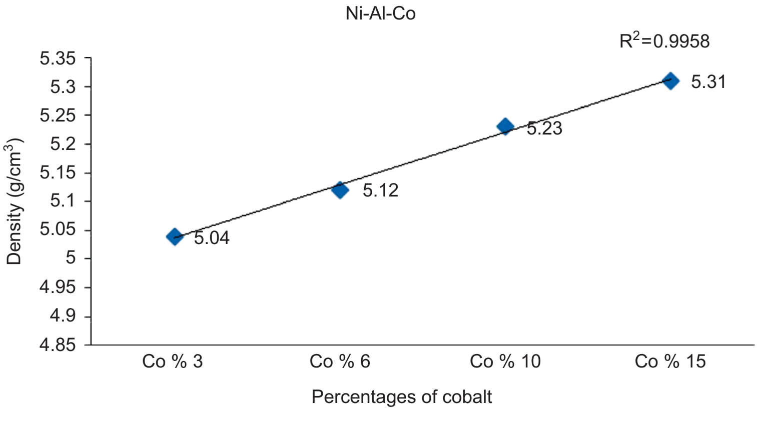

**Figure 1** Density results from Ni+Al+Co composite materials.

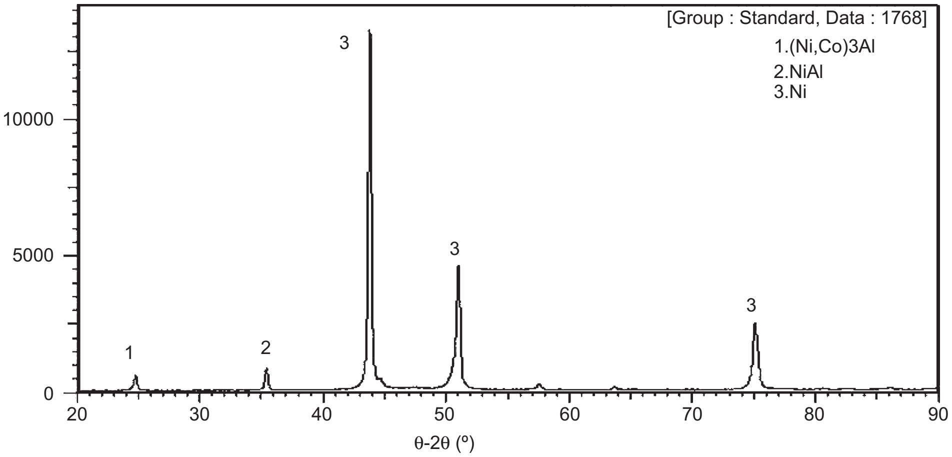

**Figure 2** X-ray diffraction (XRD) graphic of Ni+Al+3% Co composite material.

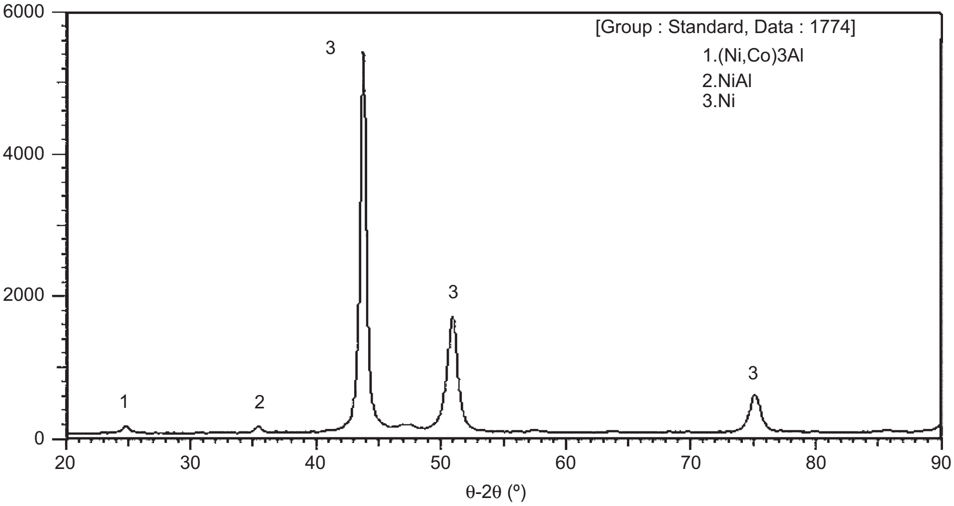

**Figure 3** X-ray diffraction (XRD) results from Ni+Al+15% Co composite.

intermetallics phase zones between the elements should be affected by the amount of Co addition into Ni+Al+Co composites. In alloy systems, Co improves the bonding by acting as metallic solvent between Ni, Al and Co particles due to having high solubility limit for Ni and limited solubility doe Al, which improve the hardness and shear strength values dramatically (FTC Lima, 2005). Hence, the solvent effect of Co should be effective between Ni, Al and Co particles in this system, as seen in Figures 2 and 3.

## 3.2 Physical characterization of sintered specimens

The densities of the samples obtained after sintering are given in Figure 1. It can be understood from Figure 1 that the highest density was obtained as 5.31 g/cm$^3$ for 15 at % Co added powder mixture, whereas the lowest density was 5.04 g/cm$^3$ for 3 at % Co added powder mixture. The difference in densities of Ni and Co are very small ($d_{Ni}$ is 8.9 g/cm$^3$ and $d_{Co}$ is 8.7 g/cm$^3$) and trendline prediction term $R^2$ value indicates that the addition of Co to the powder mixture contributes linearly to the total density of samples. This suggests that the increase is due to the increase linearly. This also suggests that the increase is due to the increase in the amount of Co with respect to Ni and Al which has lower density than Co. In this study, the effect of Co on the void closing has not been studied but the formation of intermetallic phases indicates that there is a diffusion reaction zone between the contacting powders and this leads to the conclusion that densification between constituents is occurring. However, the contribution from such densification may not be high enough to affect the density calculations.

As with density values, the hardness measurements also follows an increasing trend with the addition of Co.

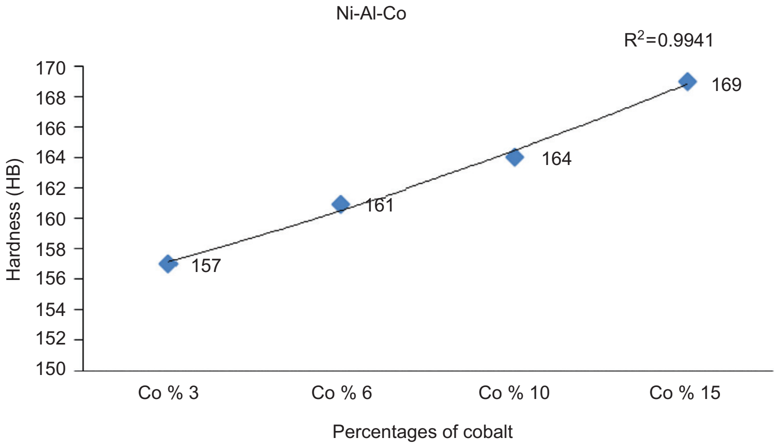

**Figure 4** Hardness results from Ni+Al+Co composite materials.

The hardness results are given in Figure 4. The hardness measurements show that the increase in Co percentage contributes towards the overall hardness of the specimens, while the highest hardness measurements were obtained with 15 at % Co addition at 169 HB, the lowest hardness measurement was obtained with the lowest Co addition, i.e., 3 at % Co at 157 HB. It can also be suggested that Co reacts with Ni and Al above 600°C and forms a strong bonding between the surrounding powders which also results in an increase in hardness in addition to the sole contribution from Co powder.

The highest shear strength value was obtained as 308 MPa in 15 at % Co added mixture while the lowest shear strength value was 279 MPa in 3 at % Co added mixture. The formation of strong bonding between Ni, Al and Co is reflected by increasing the shear strength as seen in Figure 5. However, the volume fraction of each phase is also the most important factor for determining the mechanical properties of composites in which each constituent retains most of its physical property in addition to reaction products forming during sintering. The increase in shear strength seems to be directly related to Co content by which the number of diffusion reaction zones, i.e., the volume fraction of intermetallic phase zone is increased. In alloy systems, Co improves the bonding by acting as metallic solvent between Ni, Al and Co particles due to having a high solubility limit for Ni, which improves the hardness and shear strength values dramatically [30]. Hence, the solvent effect of Co should be effective between Ni, Al and Co particles as seen in Figures 1 and 4.

## 3.3 Microstructural study

Figures 6 and 7 show SEM images from joints produced using Ni+Al+ 3 at % Co and Ni+Al+ 15 at % Co composites and S2 and S28 brazing alloys. Figures 6A,B and 7A,B show braze-composite interface from Ni+Al+Co-S2 and S28 brazing alloy joint performed in a traditional furnace

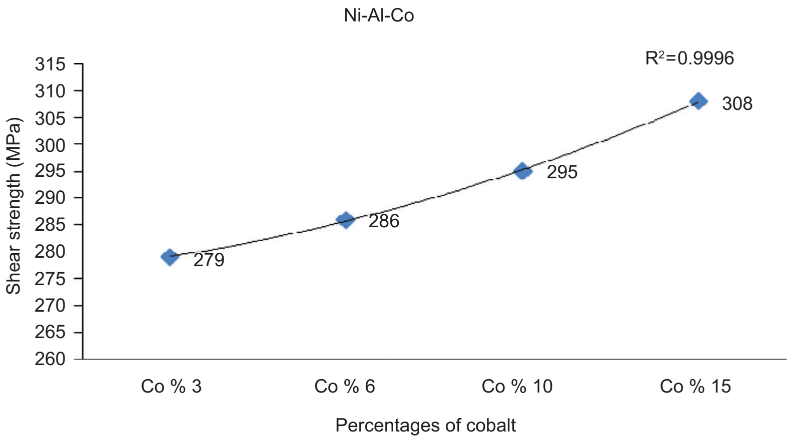

**Figure 5** Shear strength curve against the percentage of Co addition.

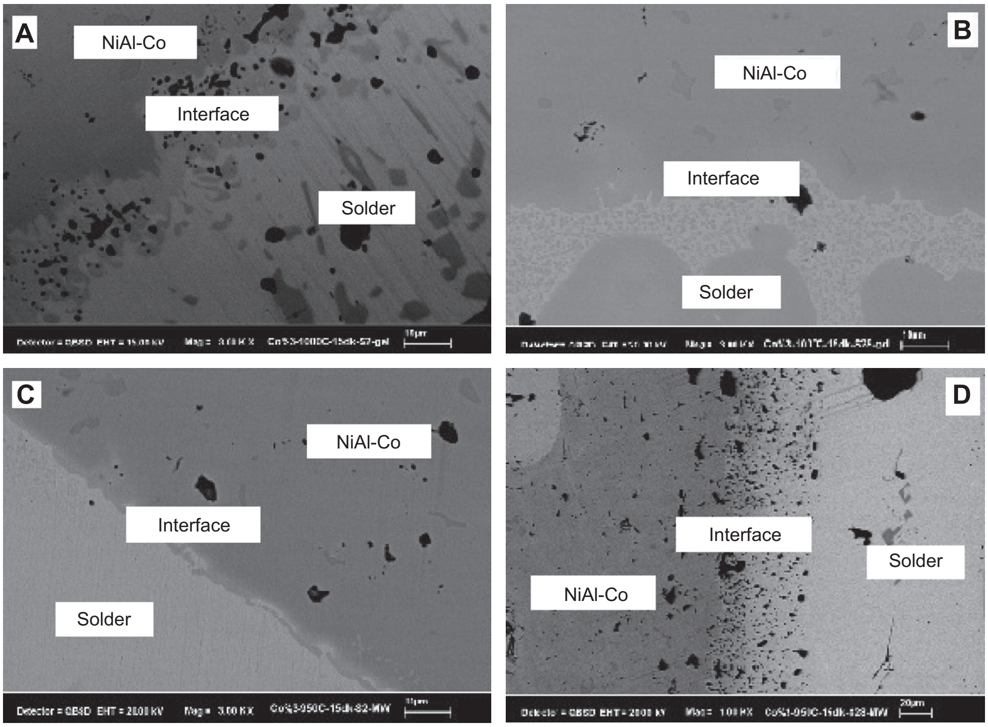

**Figure 6** SEM images from Ni+Al+% 3 Co brazed for 15 min. (A) Braze-composite interface in a traditional furnace with a S2 brazing alloy; (B) braze-composite interface in a traditional furnace with a S28 brazing alloy; (C) braze-composite interface in a microwave furnace with a S2 brazing alloy; (D) braze-composite interface in a microwave furnace with a S28 brazing alloy.

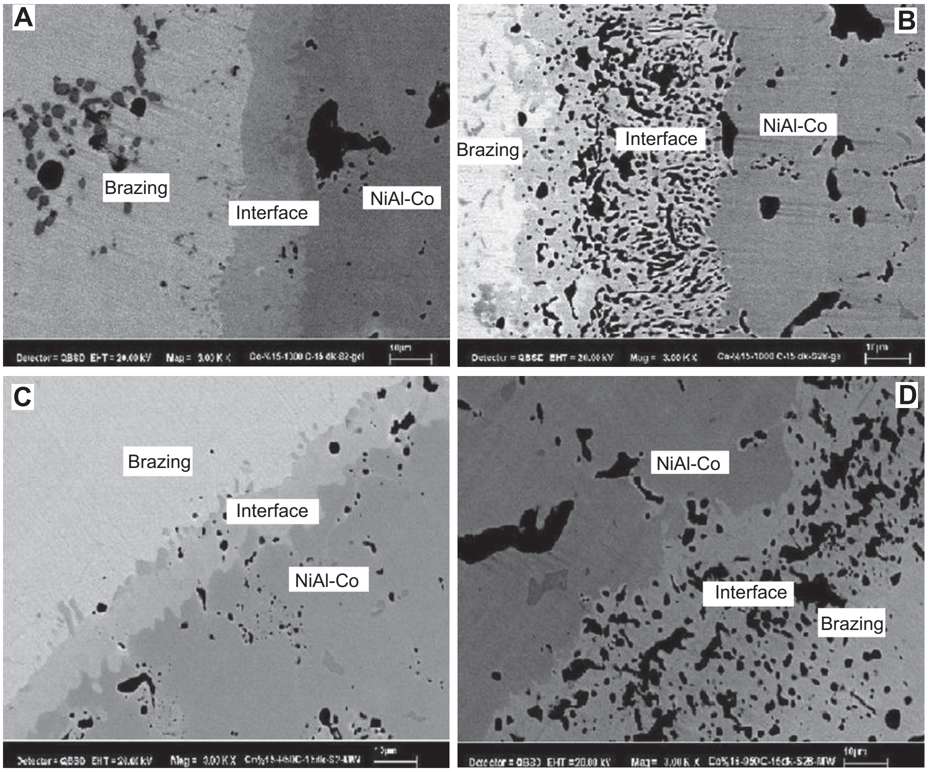

**Figure 7** SEM images from Ni+Al+% 15 Co brazed for 15 min. (A) Braze-composite interface in a traditional furnace with a S2 brazing alloy; (B) braze-composite interface in a traditional furnace with a S28 brazing alloy; (C) braze-composite interface in a microwave furnace with a S2 brazing alloy; (D) braze-composite interface in a microwave furnace with a S28 brazing alloy.

brazed at 1000°C for 15 min. This temperature is 100°C higher than the melting temperature of brazing alloy. The reason for this is to ensure melting and allow fast diffusion of alloying elements in the brazing alloy between the mating surfaces. Figures 6C, D and 7C, D show braze-composite interface from Ni+Al+Co-S2 and S28 brazing alloy joint from a microwave furnace brazed at 950°C for 15 min. Brazing temperature of the microwave furnace process is less than the traditional furnace because heating kinetics in a microwave furnace is higher than traditional one. The brazing process was successfully completed but the resultant interface or neighboring regions contained some defects such as voids, resulting from the porous nature of mating surfaces, in addition to the use of flux containing distilled water applied prior to brazing. This defect was not resolved despite using flux paste suitable for the brazing alloy. It was seen that the effect of the heating type is not important for the presence of voids. As seen in Figures 6A and B, diffusion reaction zones are visible in all specimens allowing the formation of an interface between the brazing alloy and the Ni+Al+Co composite that ensures the joining of two mating surfaces. The thickness of the reaction diffusion zone or interface in Ni+Al 3 at % Co appears to be less than that of Ni+Al+ 15 at % Co. The effect of heating on the thickness of interface in both specimen groups (i.e., 3% and 15% Co) is more obvious in Figures 7A, C and 6A, C, i.e., the effect of brazing alloy type. However, Figures 6B, D and 7B, D do not clearly show the effects of brazing alloy and heating type as they contain large voids distributed along the interface that hinders the interface characteristic. It is clear that approximate volume fractions of voids and defects present at interfaces formed by the S28 brazing alloy in Figures 6B, D and 7B, D are relatively higher than those formed by S2 type brazing alloys.

In order to understand the mechanism of alloy formation in the joint zone, EDX line analysis was made

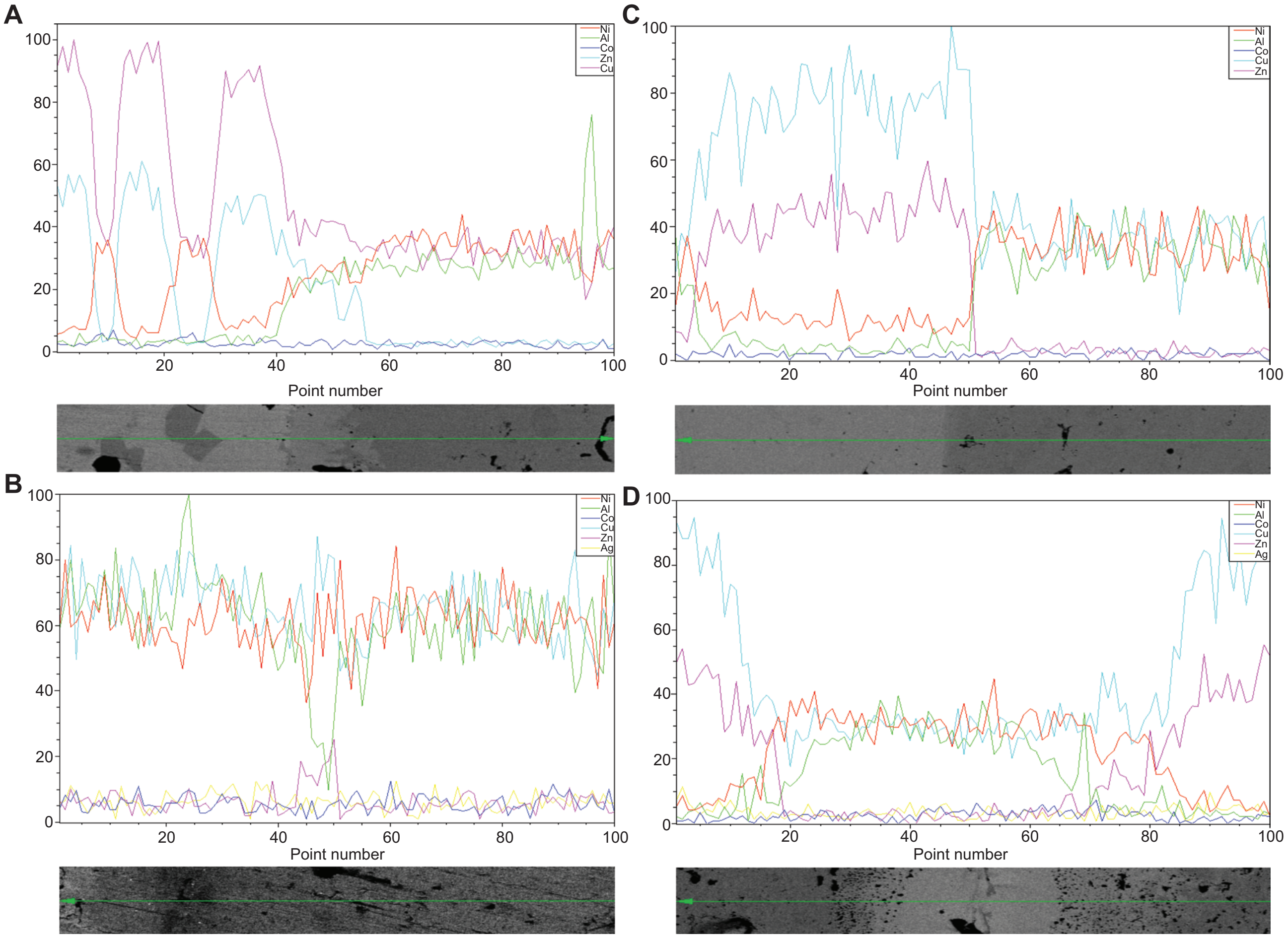

**Figure 8** EDX line analysis images from Ni+Al+% 3 Co brazed for 15 min. (A) Traditional furnace with a S2 brazing alloy; (B) traditional furnace with a S28 brazing alloy; (C) microwave furnace with a S2 brazing alloy; (D) microwave furnace with a S28 brazing alloy.

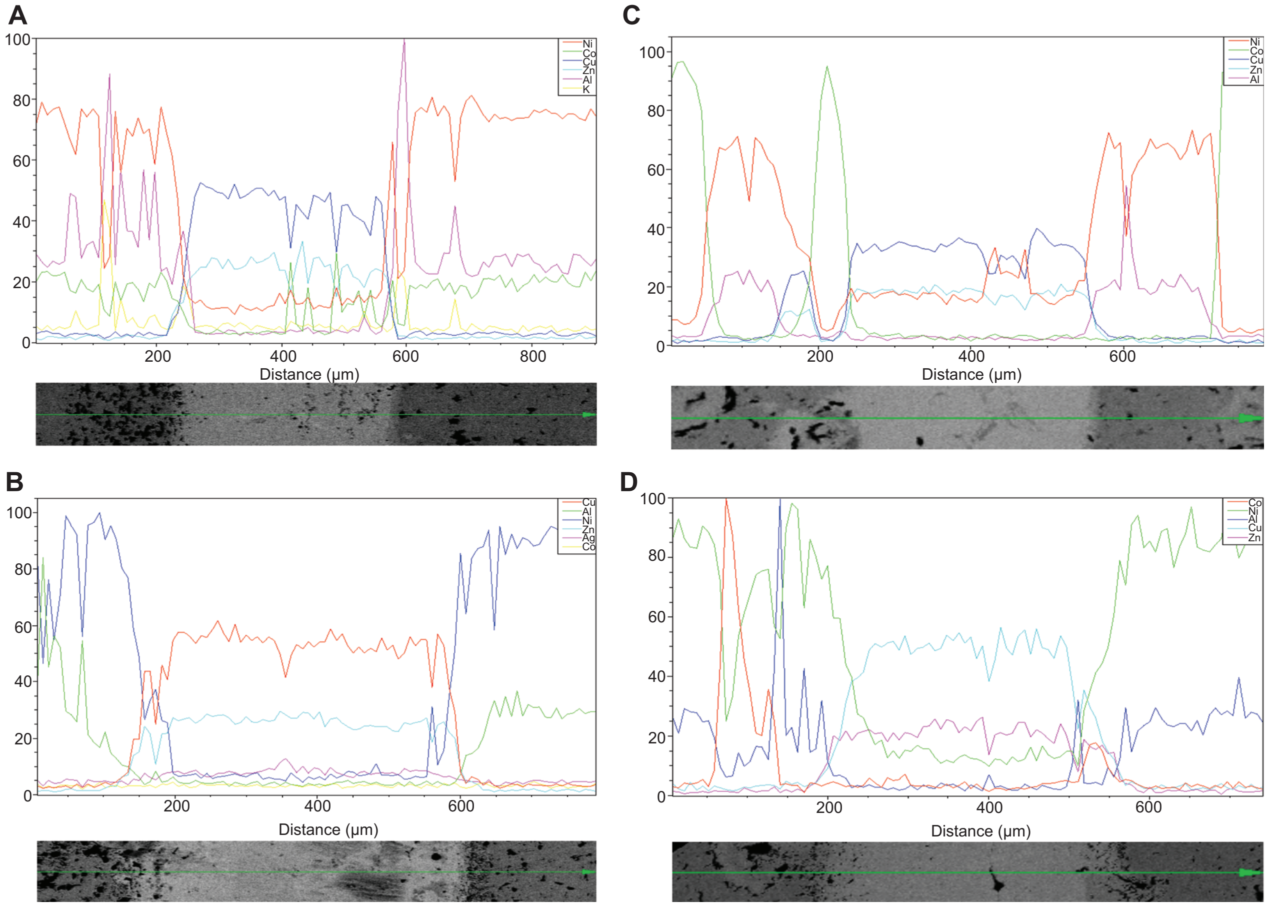

**Figure 9** EDX line analysis images from Ni+Al+% 15 Co brazed for 15 min. (A) Traditional furnace with a S2 brazing alloy; (B) traditional furnace with a S28 brazing alloy; (C) microwave furnace with a S2 brazing alloy; (D) microwave furnace with a S28 brazing alloy.

on all specimens (Figures 8 and 9). S2 and S28 brazing alloys consist of 60% Cu, 40% Zn and 60 wt% Cu, 38 wt% Zn and 2 wt% Ag alloying elements. The heating type has a pronounced effect on the alloying element distribution in brazing joint, such that the segregation is less compared to a traditional type furnace. A homogeneous distribution of alloying elements in a microwave furnace may be due to the stirring effect of electromagnetic radiation, which moves alloying elements in the liquid. A traditional furnace, on the contrary, produced regions with a variable composition, as seen in Figures 6A, C. The interface alloy distributions are not different in Ni+Al+15 at % Co composite-brazing alloy joints. It was interesting that the joints produced with microwave heating has a homogeneous distribution with a feature of straight line while joints produced with the traditional furnace have a compositionally fluctuating feature, giving out Cu rich joints. Ni is present in all joints as the solubility of Cu is infinite in Ni. Zn, Co and Ag distributions are relatively homogeneous.

## 3.4 Shear test results

Shear strength values of the traditional and microwave furnace brazed specimens are given in Table 2. The highest shear strength value was obtained with the sample Ni+Al+15 at % Co composition joined by using a S28 brazing alloy.

**Table 2** Shear strength values of brazed samples in traditional and microwave furnaces.

| **Traditional furnace** | | | | **Co addition (at %)** |
|---|---|---|---|---|
| **Brazing alloy** | **% 3** | **% 6** | **% 10** | **% 15** |
| S2 | 154 | 119 | 50 | 178 |
| S28 | 58 | 93 | 116 | 49 |
| **Microwave furnace** | | | | **Co addition (at %)** |
| **Brazing alloy** | **% 3** | **% 6** | **% 10** | **% 15** |
| S2 | 147 | 68 | 81 | 117 |
| S28 | 75 | 114 | 90 | 145 |

While the lowest shear strength value was obtained with Ni+Al+ 15 at % Co composite at 49 MPa. It is unclear whether the addition of Co increased the shear strength of specimens as the results are ambiguous. The data shows a scattered distribution of shear strength with respect to Co addition and the difference in strength values are relatively less between both heating methods. The effect of Ag is not seen properly and has a negative influence on strength values in traditional furnace brazing. The presence of voids and defects formed at the interface of brazed joints plays a major role in the shear strength values because of lower cross sectional areas with specimens that contain high defect fractions. In a study by Yoo et al. [31], the effect of Sn and Al in Ag-Cu-Zn brazing alloys was shown to affect the interface composition by forming precipitates. The use of brazing alloys with Sn did not lead to any formation of precipitates in their study. Zhang et al. [11] achieved 95.7 MPa shear strength by using the Ag-Cu-Zn based brazing TiC ceramic at 850°C for a 15 min period. When the shear strength results are compared, it can be concluded that the bonding is relatively successful with Cu-Zn-Sn brazing alloys using microwave furnace at lower heating temperatures.

## 4 Conclusion

The experiment results show that successful brazing using traditional and microwave radiation heating is possible with Sn or Ag containing brazing alloys at different temperatures. The use of microwave is efficient and allows the use of lower brazing temperatures compared with a traditional tube furnace that operate at high temperatures. The addition of Co to Ni+Al powder mixtures led to the formation of intermetallics as additional phases, such as NiAl and $(Ni, Co)_3Al$ within the matrix. Co addition increased the hardness and density of powder compacts achieving a density of 5.31 $g/cm^3$ with Ni+Al+ 15% Co and a hardness of 169 HB in the same composition. Shear strength values show that the addition of Co improves the shear strength values. The use of microwave heating is more effective as it allows the use of lower temperatures. In this case, it can be concluded that the microwave heating method has an advantage over traditional heating. The shear strength values are mostly higher in a microwave furnace than a traditional one with Cu-Zn-Sn brazing alloys. The effect of Ag is evident in this study.

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