Electro-deposited Multi-layer Metallic Coatings to Facilitate Brazing for Aerospace Applications

Prakher Gupta*, S Dhanya Chandran, PK Jayan, T Venkateswaran, Jacob Philip, Shibu Gopinath, Roy M Cherian
Materials and Mechanical Entity, Vikram Sarabhai Space Centre, Indian Space Research Organisation, Thiruvananthapuram, India-695021
Corresponding author: E-mail: prakher_gupta@vssc.gov.in; prakhergt@gmail.com Tel.:+91-8089686321, 9450139294

DOI: 10.3578/jecsi .68.1&2.2019.44

Abstract

Brazing is a widely used metal joining process, in which two or more metal parts are joined together by melting of brazing alloy. Wide variety of alloys are being used as filler metals for brazing, generally in the form of foil, rod, powder, paste, etc. This paper describes the study conducted to establish a technology to use electro-deposited multi-layer metallic coatings of copper and silver to replace copper-silver alloy foils in brazing of dissimilar metals, viz. stainless steel (SS) and copper alloy. This technology is very useful for joining parts of intricate geometry with in-built cooling channels and also for automated furnace brazing, wherein normally foils are placed on the mating surfaces beforehand, for brazing purpose.

In this study, brazing of SS to copper alloy was attempted using electroplated multi-layers of nickel (3-7μm) and copper (22-30μm) on SS and copper (20-27μm) and silver (12- 18μm) on copper alloy. The reaction that takes place between these layers during brazing is expected to result in the formation of in-situ braze metal. For establishing this technology, extensive coating and brazing trials were carried out on flat specimen for microscopy and flat lap-shear coupons. After coating and brazing, flat specimen used for microscopy and lap-shear specimens were tested for bond strength evaluation and the quality of the braze-joint. The paper describes these functional tests along with the standard qualification tests conducted to ascertain the quality of the electrodeposited coatings.

Keywords: Electroplated multilayer Nickel, Copper, Silver, coating, braze foil, brazing-through-coating route,

1. Introduction

Silver and Copper are widely used in various applications, owing to their physical and mechanical properties, such as aesthetics in jewelry; electrical and thermal conductivity in electronic semiconductor packages, thermal properties for power generation and hydraulic systems; malleability and low resistance for making bonded thin wires, etc. Apart from such applications, the copper-silver multilayer coating is proposed to be used in metal joining for aerospace applications. This paper describes the study conducted to establish a technology to use electro-deposited multi-layer metallic coatings of copper and silver, to replace copper-silver alloy foils in brazing of dissimilar metals, viz. stainless steel (SS) and copper alloy. This technology is very useful for joining of parts of intricate geometry with in-built cooling channels and also for automated furnace brazing, wherein normally foils are placed on the mating surfaces beforehand for brazing purpose.

In this study, brazing of SS to copper alloy was attempted using electroplated multi-layers of nickel (3-7μm) and copper (22-30μm) on SS and copper (20-27μm) and silver (12- 18μm) on copper alloy. The reaction that takes place between these layers during the brazing is

expected to result in the formation of in-situ braze metal. For establishing this technology, extensive coating and brazing trials were carried out on flat specimen for microscopy and flat lap-shear coupons. After coating and brazing, flat specimens were used for microscopy and lap-shear specimens were tested for bond strength evaluation and quality of the braze-joint. The paper describes these functional tests along with the standard qualification tests conducted to ascertain the quality of the electrodeposited coatings.

2. Experimentation

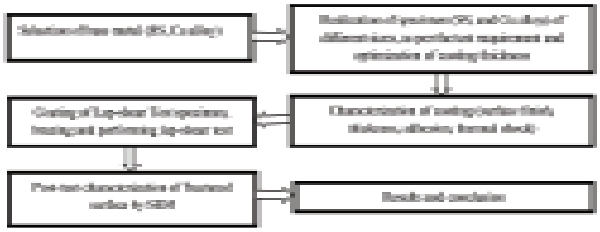


Fig.1: Flow chart for electroplated multi-layer Silver and copper coating for replacement of braze foil

The aim of the study is to establish a technology by which electro-deposited multilayer of silver and copper combination replaces the braze foils and produces the in-situ braze metal to join two alloys, the plan of action is shown in fig.1. For this SS and copper alloy were selected as substrate pair, which is extensively used in aerospace industry. Eight pairs of coupons of both the alloys were realized. Prior to actual coating, SS specimens were given an under coat of nickel by Wood's bath. Subsequently, nickel coating was given from a Watt's bath prior to copper coating. By providing a thin layer of Nickel coating on the base metal, complete wetting of the surface and spreading of braze metal on the base metal was ensured. Apart from this, Nickel coating functions as a barrier coating and helps in reducing inter-granular penetration of braze metal into the SS base metal. Coating was carried out on the coupons as per the scheme shown in Fig.3 and qualified by a test plan and the results are discussed subsequently.

2.1 Substrate Selection

The chemical composition of the base materials viz. Stainless Steel (SS) and copper alloy is listed in Table 1 and Table 2, respectively. Stainless Steel (SS) base metal properties listed correspond to hardened (750ÚC/1hour/air cooled) and aged (at 500ÚC for 2 hours) condition, whereas those of copper alloy correspond to solution-treated (at 985ÚC for 15 minutes) condition [1].

2.2 Preparation of flat specimen for coating optimization and Specimen for lap-shear tensile test for brazing

Coupons of both base metals of size 28.5 x 28.5 x 3 mm were used for microscopy and of size 127 x 28.5 x 3 mm were used for lap-shear testing with 10mm width plating area and as shown in Fig.2 (a) and 2(b).

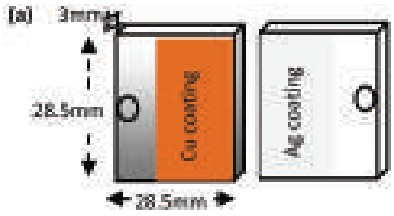


Table 1: Base metal composition of Stainless Steel (SS)

Alloying elements	C	Cr	Ni	Mo	Ti	Fe
Composition (% Wt)	0.03(max)	12.1	9.8	0.7	0.2	Bal.

Table 2: Base metal composition of copper alloy

Alloying elements	Cr	Zr	Ti	Cu
Composition (% Wt)	0.56	0.032	0.028	Bal.

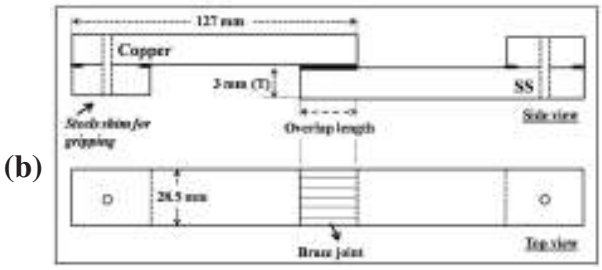


Fig.2: Schematic of (a) flat specimen (b) Lap-shear test sample for coating on Steel (Ni 5µm and Cu 25µm) coating and copper alloy base materials (Cu 25 µm and Ag 13µm).

2.3 Cathode substrate pre-treatment

2.3.1 Pretreatments for SS: Before plating on SS specimens of size 28.5 x 28.5 x 3mm, standard pre-cleaning procedures were adopted. The processes followed for pre-cleaning were solvent and vapour degreasing at 85°C for 25sec. with Trichloroethylene (TCE), hot caustic dip, acid pickling in 10% (by vol.) hydrochloric acid (10sec). Surface was activated by a dip in hydrochloric acid. It was then rinsed and subjected to Wood's nickel undercoat, as given in Table 3.

2.3.2 Pretreatments for Copper alloy: Prior to plating, flat copper alloy specimens of size 28.5 x 28.5 x 3mm was mechanically polished, degreased and vapour degreased and then subjected to caustic dip, acid pickling as mentioned in 2.3.1. It was followed by rinsing prior to copper electroplating.

2.4 Electroplating process

All Coatings were carried out by electroplating process. Multi-layers of nickel (thickness 3-7µm) and Copper (thickness 22-30µm) provided on SS. On copper alloy, multi-layers of Copper (thickness 20-27µm) and Silver (thickness 12-18µm) were provided. The coating scheme is shown in Fig. 3(a) and 3(b). The process parameters used for electroplating of Ni, Cu, and Ag are provided in Table 3 [2]. Before electroplating, the base metal coupons were appropriately masked to allow coating formation selectively in the areas where it is required, as shown in Fig. 3 (a) and 3(b)

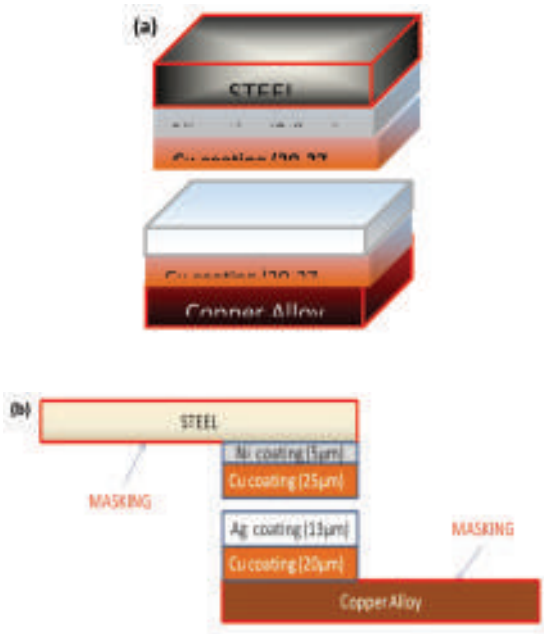


Fig.3: Schematic of scheme (a) flat specimen and (b) Lap-shear test samples for coating on Steel (Ni 5µm and Cu 25µm) coating and copper alloy base materials (Cu 25 µm and Ag13µm).

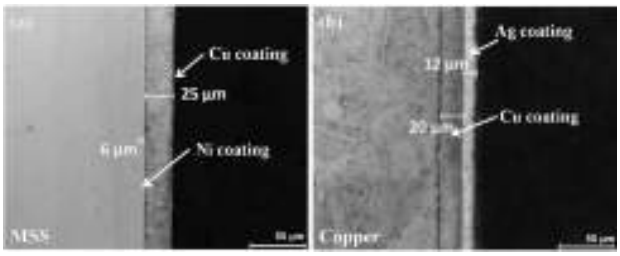


Fig.4. Cross-sections of coated specimen with layers of Ni, Cu, and Ag (a) SS and (b) copper alloy base materials

The mating surfaces of the SS and copper alloy flat specimen as well as Lap shear test coupons were coated with the respective metals by electroplating process, as per the scheme given in Fig.3 (a) and 3(b). The coated specimens are shown in Fig. 5(a) and 5(b). The thickness of Cu and Ag coatings achieved was uniform on both the base materials as shown in Fig.4.



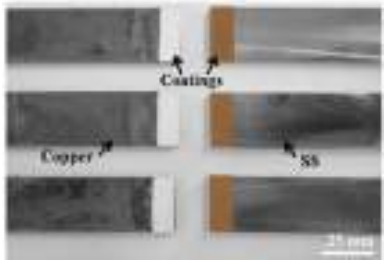
(b) 

Fig.5: (a) coated flat specimen (b) flat lap shear specimen with Ni 5µm and Cu 25µm coating copper alloy with Cu 25µm and Ag13µm.

3. Coating characterization

3.1 Micro-structure and surface roughness

Detailed examination of the microstructure of base materials and electroplated and brazed samples were carried out using optical microscope (OM, Carl Zeiss-Axio Lab.A1). A few selected samples were taken for further detailed studies using the Scanning Electron Microscope (SEM, Tescan Vega 3). The surface roughness achieved after brazing was evaluated using surface roughness analyzer (Formtaly surf PGI800).

3.2 Visual and Micro-structural observation

The coating was visually observed for its colour, continuity and smoothness. Adhesion test was done before and after thermal shock test, by visual observation followed by tape test. Morphology of the braze joint was assessed by scanning electron microscopy (SEM) and the coating thickness was evaluated by optical microscopy on the cross-section of samples.

3.3 Tape test

It was done using a 25 mm wide semi-transparent, pressure sensitive adhesive tape (3M make, type 250YT). The tape segment of length ~70 mm was placed over a clean dry area of the coated coupon. It was smoothened to avoid ensuring that any wrinkles and air bubbles. The free end of the tape was pulled off swiftly without breaking it. The area was inspected for any debond of the coating.

Table 3: Details of electroplating bath composition and process parameters used to coat Ni, Cu, and Ag coating

S.No.	Bath type	Electrolyte Composition	Temperature (°C)	Anode to Cathode ratio.	Current density (A/dm^2)	Rate of deposition (µm/min)
Nickel coating						
1	Wood's Bath	$NiCl_2$: 240g/L $NiSO_4$:250ml/L	RT	Ni anode (1:1)	12	1 to 2
2	Watt's Bath	$NiCl_2$: 45g/L $NiSO_4$:312ml/L H_2BO_3: 37.5g/L	45-60		8	1.3
Copper coating						
3	Copper coating Bath	$CuSO_4.5H_2O$: 220g/L H_2SO_4: 38.5ml/L NaCl: 0.16 g/L Additive	RT	Cu anode (2:1)	4	0.7
Ag coating						
4	Silver Coating Bath	Bright silver salt :200 g/L Brightner: 30ml/L Additive: 10ml/L	RT	Ag anode (1:1)	1	0.5

3.4 Thermal Shock test/Adhesion test



Schematic block diagram for adhesion test procedure

Surface of the coated coupons was again checked with 4X magnification to ensure absence of any surface defect. Before Thermal shock, the tape test was repeated. The coupon was undergone standard thermal cycling as per Table 4. After completion of thermal shock test, visual observation and tape test were repeated. No debond/crack of film indicates good adhesion of coating[2].

Table 4: Operating parameters for Thermal cycling

Parameters	Value
Lower temperature	-60°C
Higher temperature	180°C
No. of Cycle	15
Soaking time	10 min
Approx time (total)	6-8 hrs

3.5 Brazing process

Flat coupons and lap-shear test samples were prepared as per the coating scheme shown in Fig. 3(a) and 3(b), respectively. After coating these coupons/samples were brazed in a vacuum brazing furnace (chamber size: dia. 500 x 500(L) mm, vacuum up to 10^{-4} mmHg, temperature up to 2000° C, Make: Hindby Ltd) applying the dead load over the lap area. Brazing of these flat coupons was carried out as per brazing cycle as shown in Fig.6 at 985ÚC for 15 minutes [3-7]. The brazing fixture used in these experiments was fabricated using Inconel 718 alloy, to hold the two plates in position during brazing.

A torque of approx 12-15Nm was applied in the lap area by tightening with the help of two M6 bolts, to ensure the required contact pressure.

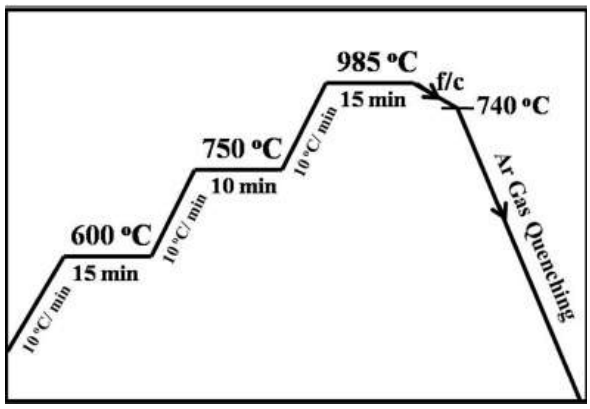


Fig.6: Schematic of the brazing cycle used

3.6 Mechanical property evaluation

Testing of lap-shear and tensile test samples (exposed to brazing thermal cycle) were carried out using a Universal Testing Machine (UTM, Zwick/Roell 1475, 100kN). Tensile properties of the base materials were also evaluated before and after brazing thermal cycles. Microstructure analysis of the fractured lap-shear samples was performed using SEM [8].

4. Results and discussion

4.1 Base materials

SS base metal used in this study, under fully heat treated condition, exhibited 0.2% Yield Strength (YS) of 988 ± 8 MPa, Ultimate Tensile Strength (UTS) of 1035 ± 8MPa and % elongation (El.) of 19.5 ± 1. Fig. 7(a) shows the optical micrograph of the SS base metal. The presence of prior-austenitic grain boundaries with lath type martensite is evident from this microstructure.

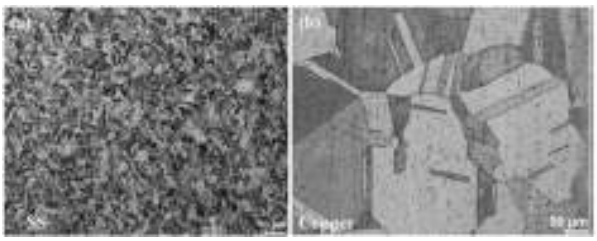


Fig.7. Optical micrographs of (a) SS and (b) copper base materials

The second base metal, copper alloy in solution heat treated condition showed 0.2% YS of 85 ± 5 MPa, UTS of 240 ± 6 MPa, and % El. of 51 ± 2. Fig. 7(b) shows the optical micrograph of the

copper alloy base metal. The microstructure of this copper base metal is characterized by the presence of annealed grains of different aspect ratio, with annealing twins.

4.2 Multilayer electro-deposition of Ni, Cu, and Ag

A continuous, smooth and intact coating, free from any visual defects like, blisters, uncoated areas, flaking, roughness, cracks or pits was obtained. Coating roughness was noticed at the substrate edges and the deposition rate was also found to be marginally higher at this area, compared to the centers. The surface morphology at the middle of the coupon surface was therefore critically observed. The thickness of the multilayer coating on SS and copper alloy was measured by the microscopic examination of cross sections using an optical microscope is presented in Fig. 4. Thickness of Ni coating employed was 5ìm nominal, against the indented thickness of range of 3-8ìm and was found to be uniform across the cross-section of the SS base metal. A typical cross-sectional optical micrograph of SS and copper alloy base metal with a respective coating are shown in Fig. 4. Coating thickness of silver was 12ìm against the indented range of 12-18ìm. The coating was found to be uniform across the base metal. However, the surface roughness was on the higher side as compared to Ni and Cu coatings. This is not a major concern, as these inter-layers are going to react and form the braze metal during brazing.

The SEM micrographs of the SS/copper alloy braze joint are shown in Fig.8. It is clear from these figures that the solidified braze metal consists of two distinct features: one is a Cu-rich primary alpha (áP) phase, and the other is a eutectic mixture. This eutectic composition consists of an Ag-rich beta phase (â) and a Cu-rich eutectic alpha phase (áE) and it is located in the middle of the braze metal between the áP. The amount of eutectic mixture is less in case of SS/ copper alloy joint realized as per coating scheme shown in Fig.3. (lower Ag thickness). During the cooling phase of brazing, solidification of braze metal begins with the formation of áP, on the interface of base materials, with the rejection of Ag atoms at the solid-liquid interface (L [redacted] áp+ L). The solidification process of the braze metal ends up when the liquid at the interface (between áp) attains a eutectic composition (L [redacted] áE +â) at the eutectic temperature of ~779 °C, as guided by Ag-Cu binary system.

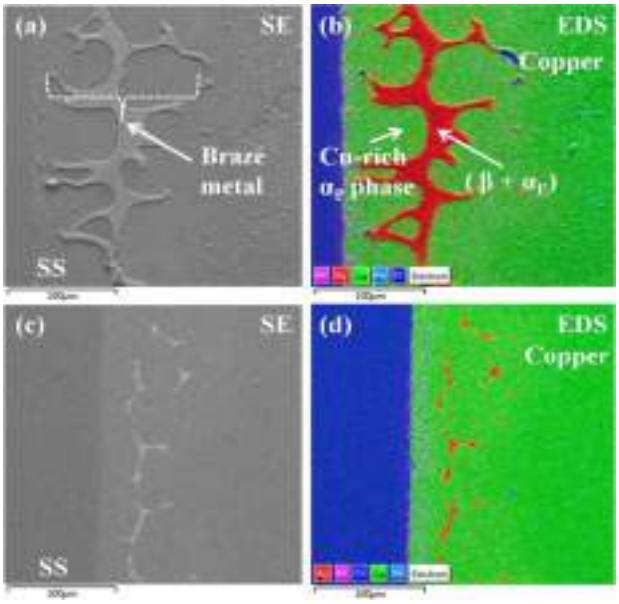


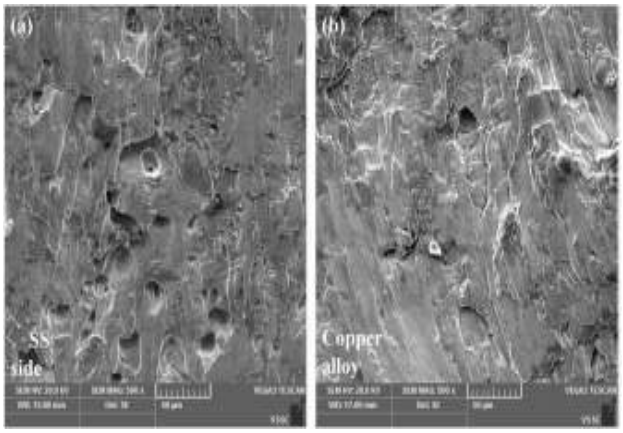
Fig.8. SEM-SE micrograph (a) and elemental maps of Cu, Ag, and Ni across the SS/copper alloy braze joint (b to d)

The phase diagram of Ag-Cu binary system is shown in Fig.9. One line is marked on the Ag-Cu phase diagram, which corresponds to the braze metal composition expected with the coating schemes employed as per Fig.3. This line is drawn with the assumption of nil diffusion and/or dissolution of copper alloy base metal. Fig.9 (c) is Ag-Cu binary phase diagram. Whereas, in actual, dissolution and diffusion are inevitable and composition of the realized braze metal may differ slightly from the predicted one [9-11]. SEM spot analysis was taken on áP and eutectic mixture of the braze metal at three different identical locations. The phase áP exhibited a composition of 7.5 wt. % Ag, 1.5 wt. % Ni, and balance Cu. Ni enrichment in the braze metal is probably due to the dissolution and diffusion of Ni from the Ni coating provided on the SS base metal. Also, this áp is found to have a small amount of chromium of about 0.2-0.3 wt. %. Dissolution of copper alloy base metal at brazing temperature is a

probable source for this chromium content in braze metal. The chemical composition of the eutectic mixture (áE + â) was Ag - 28 wt. % Cu. Unlike áP, the content of Ni and Cr in the Ag-rich phase is almost nil and it is primarily due to its limited solubility in Ag.

4.3 Lap-shear testing of SS/copper alloy joints

Lap-shear test samples were prepared as per coating schemes shown in Fig. 2(b) and Fig. 3(b) and brazed in Vacuum Brazing Furnace. The overlapping length of the lap-shear test samples was 9 mm (3T). During tensile test, failure was observed at the copper alloy base metal with a breaking load of ~19-20 kN. Subsequently, the lap-shear test samples were realized with a reduced lap length of 3 mm (1T) to get the shear strength of the SS/copper alloy braze joint, precisely. These lap-shear test samples with an overlap length of 3 mm, exhibited shear strength of 151 MPa. The above-reported values are the average of 3 samples. Fig 9 (a) and (b) show the SEM micrographs of the typical fractured surface of a lap-shear sample of SS and copper alloy, respectively. The presence of ductile shear dimples and deformed grains along the shear directions are evident from these fractured surfaces.



(c)

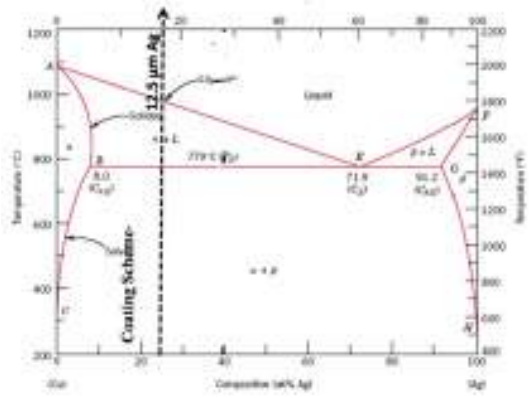


Fig.9 (a) SEM micrographs showing the fracture features of lap-shear tested SS (b) copper alloy samples and realized with an overlap length of 3 mm. (c) Ag-Cu binary phase diagram

5. Conclusions

In the present study, brazing of Stainless Steel (SS) to Copper alloy base material has been carried out using electroplated coatings of Ni, Cu, and Ag. Brazing using electroplated coatings is established as a reliable and economical manufacturing process. The following conclusions are drawn, based on the experimental results:

1. The electroplated coatings can be methods to produce in-situ braze metal through a reaction between Ag and Cu. Effect of different coating schemes (with higher and lower Ag coating thickness) was addressed in this study. All brazing experiments were performed at 985°C with a hold period of 15 minutes. Additionally, a layer of Ni coating (5 ìm) was provided on the SS base metal side to improve adhesion and wettability and to minimize the inter-granular penetration of the braze metal.

2. SS/copper braze joints produced with different coating schemes are found to be strong/intact and the failure was observed always in the copper alloy base metal at a breaking load of 19-20 kN. On average, lap-shear strength of 151 MPa was obtained for the SS/copper joint produced with an overlap length of 3 mm, as per the given coating scheme. The failed lap-shear surfaces were characterized by the presence of ductile elongated shear dimples of the braze metal.

3. The braze material consists of a Cu-rich primary alpha phase (áp), in addition to a eutectic composition (â + áE). Apart from Ag and Cu- the áp of the braze- it has a small amount of Ni and Cr content. Ni coating on SS base metal and Cr alloying element of copper alloy base metal are the sources of this enrichment. The amount of eutectic mixture in the given coating scheme is very less.

REFERENCE

[1] Sims, CH.T. Stoloff, N.S. Hagel, (1987).Superalloys II, John Wiley, Inc: USA.

[2] Prakher Gupta, R. K. Gupta et.al. Optimization of parameters for electro-deposited silver coating on Inconel 718, published in Materials today: proceedings, vol 5, issue2, part2, (2018); pp7496-7504.

[3] J. B. Mohler, (1984). Electroplating and related processes, Chemical Publishing Co., Inc.: New York.

[4] T. Fukikoshi, Y. Watanabe, Y. Miyazawa, F. Kanasaki, Brazing of copper to stainless steel with a low-silver-content brazing filler metal, IOP Conf. Ser. Mater. Sci. Eng.,(2016) 61.

[5] S.V. Lasko, N.F. Lasko, Soldering Metals, (fourth ed.), 5-217-00268-9, Engineering, Moscow (1998) (in Russian)

[6] M.M. Schwartz, Brazing, (second ed.), ASM International (2003).

[7] D.M. Jacobson, G. Humpston, Principles of Brazing, ASM International (2005).

[8] Standard Method for Evaluating the Strength of Brazed Joints, AWS C3.2M/C3.2:2008, (fourth ed.) (January 4, 2008)

[9] N. Eustathopoulos, F. Hodaj, O. Kozlova, The wetting process in brazing, Advances in Brazing, Woodhead Publishing Ltd., (2013) 3-30.

[10] O. Kozlova, R. Voytovych, M. Devismes, N. Eustathopoulos, Wetting and Brazing of Stainless Steels by Copper-Silver Eutectic, 495 (2008) 96–101.

[11] P.R. Subramanian, J.H. Perepezko, The Ag-Cu (silver-copper) system, Journal of Phase Equilibria, 14 (1993) 62-75.