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SEM-EDS Analysis and Microhardness Variations in Steel-Copper Braze Joint

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***Abstract* — This research paper reports the scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDS) analysis and microhardness variations in a stainless steel-copper braze joint. The brazing of copper with stainless steel has been performed at temperatures in the range of 640-680 °C for the time durations in the range of 5-15 min by using a copper-based brazing filler metal (BFM) under an argon gas atmosphere in a brazing furnace. Material's chemistry of brazed samples has been studied by energy dispersive spectroscopy (EDS) system linked with a Phenom Pro X scanning electron microscope (Phenom Pro SEM). It has been found that Ni atoms from the BFM diffused into stainless steel owing to the better solid solubility of Ni in Fe than that of Cu in Fe. A low Sn at.% was observed in the EDS image for BFM region; this elemental distribution has been attributed to the possibility of reaction of Sn with Fe to form an intermetallic compound: FeSn2. The spatial distribution of various elements has been studied by mapping analysis by using SEM-EDS technique for a brazed sample that showed the penetration depth of Ni and P to stainless steel and copper regions. Microhardness measurements at various locations of the brazed sample have been made and analyzed. The microhardness data has been graphically analyzed and related to brazing parameters.**

***Keywords*— Copper • stainless steel • brazing • SEM-EDS • elemental distribution • mapping • microhardness**

I. INTRODUCTION

The study of microhardness variations and element distribution mapping is of great technological importance since many materials properties are strongly dependent on hardness and compositional homogeneity [1-2]. The stainless steel-copper braze joints find extensive applications in heat exchangers, refrigerators, and electronics. In particular, several factors must be considered in selecting a combination of materials for a heat exchanger; these factors include: corrosion resistance, strength, heat conductivity, and cost [3]. Copper has high thermal conductivity whereas stainless steel (SS) has excellent strength with a good stiffness. The mechanical behavior of a braze joint strongly depends on the elemental distribution within the brazed region. This is why, the study of elemental distribution and microhardness of braze joints is of great importance in a welding/joining industry. This technological importance motivated the author to conduct a research and report it as the present paper.

The elemental distribution in a specified region in a material can be analyzed by using energy dispersive X-ray spectroscopy (EDS); which makes use of the X-ray spectrum emitted by a solid sample bombarded with a focused beam of electrons to obtain a localized chemical analysis. By scanning the beam in a television-like raster and displaying the intensity of a selected X-ray line, element distribution images or 'maps' can be produced [4]. Although, a scanning electron microscope (SEM) is primarily designed for producing electron images, it can also be used for elemental mapping, and even point analysis, provided an X-ray spectrometer is added [5]. In EDS, the relative intensity of an X-ray line is approximately proportional to the mass concentration of the element concerned. Thus an *apparent concentration* (*C′*) of an element can be expressed by the following relationship [6]:

$$C' = \frac{I_{sp}}{I_{st}} C_{st} \qquad (1)$$

where I_{sp} and I_{st} are the intensities measured for specimen and standard, respectively; and C_{st} is the concentration of the element concerned in the standard.

Zaharinie and co-researchers (2015) have studied the chemistry of Cu-Cu braze joint produced by use of a copper-based brazing filler metal (BFM) [7]. The EDS point analysis of the braze joint showed the composition of a point conforming to 85Cu-8.3Sn-5.7O-1P; which referred to the two-phase field: (1) solid solution of tin and phosphorous in copper; and (2) the copper oxide: Cu_2O. The EDS data for the braze joint showed a large variation in the alloying element contents; which was justified by the possibility of formation of solid solution of Sn and P as well as hard phases, including the intermetallic compound: Cu_3P. In particular, the formation Cu_3P is believed to impart a good strength in the joint [8].

Fukikoshi and co-workers (2014) have investigated brazing of copper to stainless steel by using a low-silver content BFM [9]. They have shown that a dissolution reaction occurred at the copper side when the low-silver-content BFM was used. In contrast, molten silver-based BAg8 penetrated along the crystal grain boundary of the copper base metal when BAg8 BFM was used. Penetration of the molten BAg8 filler along the crystal grain boundary was caused by the dissolution of Ni from the stainless steel into the molten filler [9].

The determination and analysis of microhardness at various point locations of a braze joint is also important since they enable us to assess the strength and wear resistance of the joint. Microhardness is generally measured by a Vickers micro-hardness tester. Vickers hardness (HV) can be calculated by the following formula [10]:

$$\mathrm{HV} \cong 1.854 \frac{F}{d^2} \qquad (2)$$

where F is the applied load, kgf; and d is the arithmetic mean of the two diagonals of the square indentation, mm. Recently

(2018), Jiang and co-workers have reported microhardness of WC-15Co/35CrMo braze joint to be in the range of 2341-2693 MPa (239-275 kgf/mm^2); the joint was produced by using a silver-based alloy as the brazing filler metal (BFM) [11].

II. Experimental Work

Materials/Sample Preparation. The work-piece sample was prepared by considering the configuration for the top and base metal with the location for the filler metal. Commercially pure copper and SUS304 stainless steel were used as the base materials. The chemical compositions of these metals are presented in Table 1 [9].

Table 1: Chemical compositions (wt. %) of the base metals

Material/Elements	Cu	P	Fe	C	Si	Mn	S	Ni	Cr
Copper	99.96	0.02	-	-	-	-	-	-	-
SUS304 stainless steel	-	-	Bal.	0.04	0.59	0.28	0.003	9.13	18.2

In the present research, VZ2250 was used as a brazing filler metal (BFM); which is a copper-based metal developed by the company: VACUUMSCHMELZE. The chemical composition of VZ2250 is as follows: Cu-7Ni-9.3Sn-6.3P. The 40-µm thick BFM used was cut into a size of 10 mm x 10 mm. The copper and stainless-steel sheets were cut into the sizes of 30 mm x 10 mm each so as to develop the single-lap specimen.

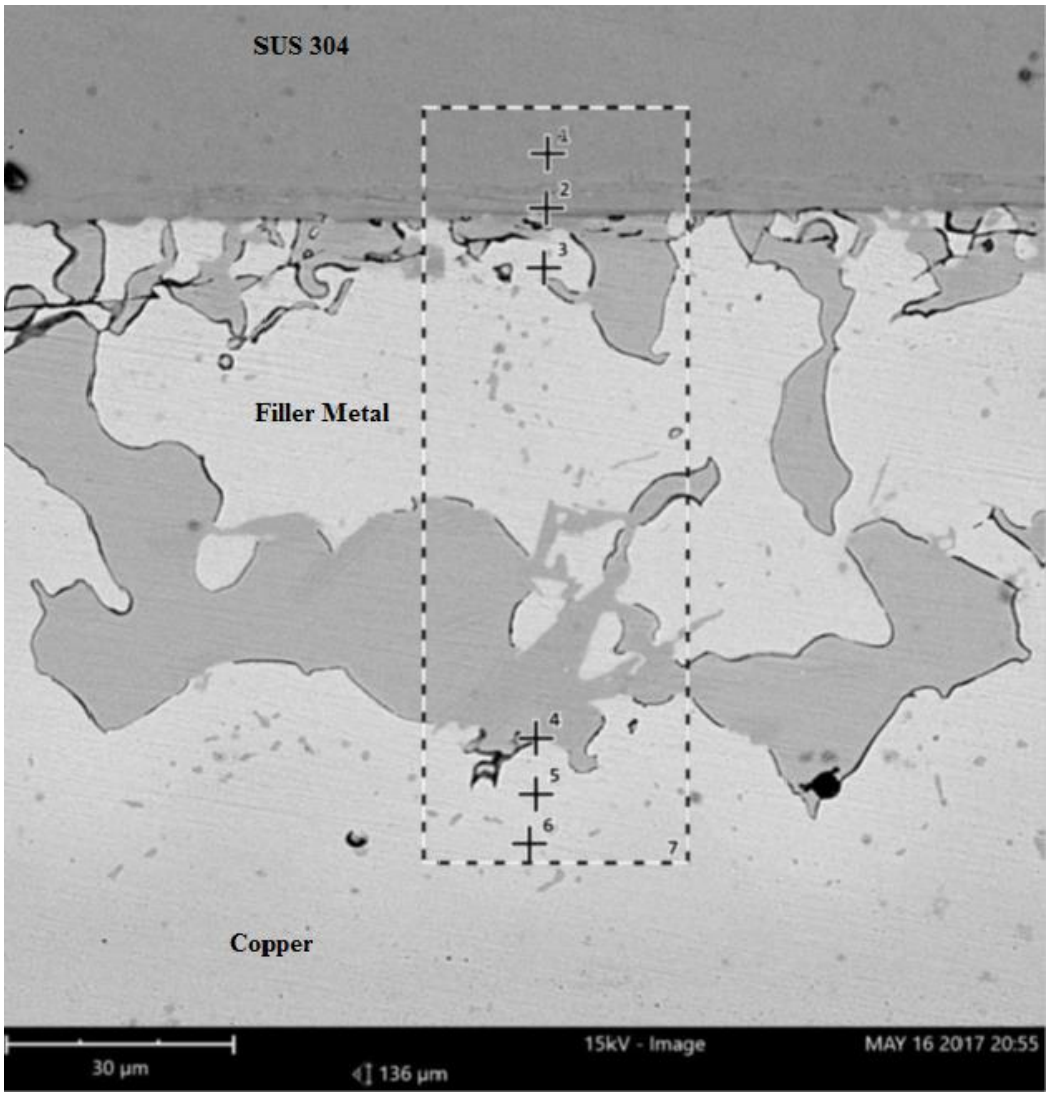


Fig 1. EDS marking area on the SEM micrograph for the brazed sample: 660°C, 15 minutes

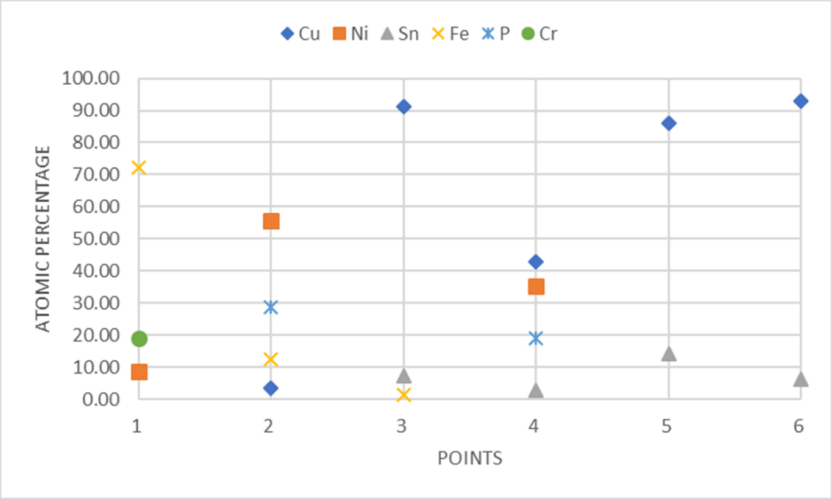


Fig 2. EDS result for average atomic % for various elements

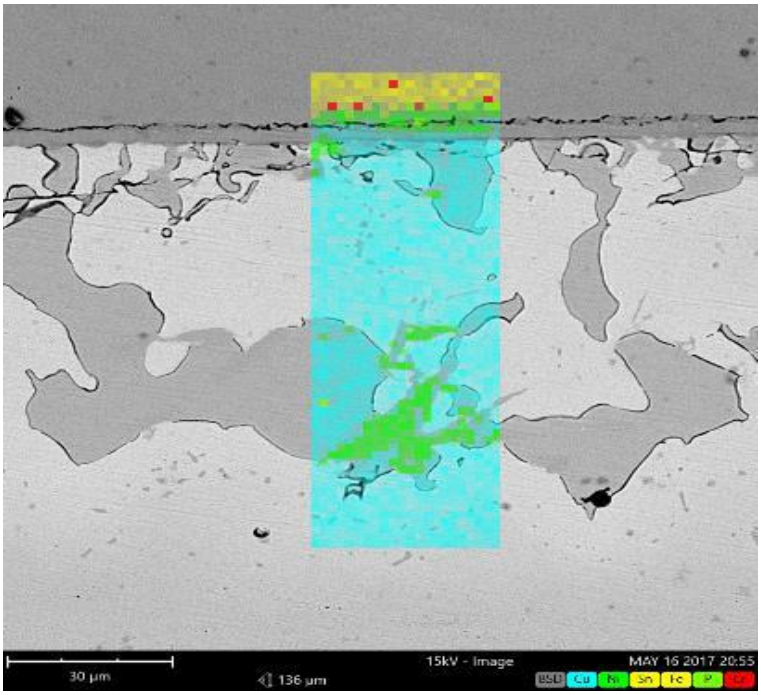


Fig 3. Mapping analysis by SEM-EDS for the sample brazed at 660°C/15 min

The Brazing Process. An argon-gas atmosphere-controlled tube furnace was used for the brazing experiment [12]. The optimum heating/cooling rate of the tube furnace (KYK Model) is 10°C/min. The brazing samples were preheated at 600 °C for 10 minutes before the actual brazing operation; the pre-heating was important due to a time difference between the programmed temperature and the actual sample temperature [13]. The preheated samples were then brazed at temperatures in the range of 640 – 680°C for time durations in the range of 5-15 min.

EDS-SEM Analytical Techniques. Material characterization of braze joint involved energy dispersive spectroscopy (EDS) by use of a modern scanning electron microscope (*SEM*). This analytical technique is extensively employed for studying materials chemistry [1,14]. The energy dispersive spectroscopy (EDS) was accomplished by use of *Phenom-Pro-X* analytical system lined with an SEM so as to analyze the elemental distribution along the Cu-SUS304 braze joint. Mapped SEM micrographs were obtained by use of EDS-SEM for various brazed samples.

Mircohardness Testing. Microhardness testing for brazed samples were conducted by applying a load of 10 kgf for a duration of 10 seconds by use of a Vickers hardness micro-indenter (*Shimadzu*, HMV 2T E). Microhardness measurements were recorded at five different positions of each brazed sample; and then an average of each set of data was determined.

III. Results and Discussion

A. Energy Dispersive X-ray Spectroscopy (EDS) Analysis:

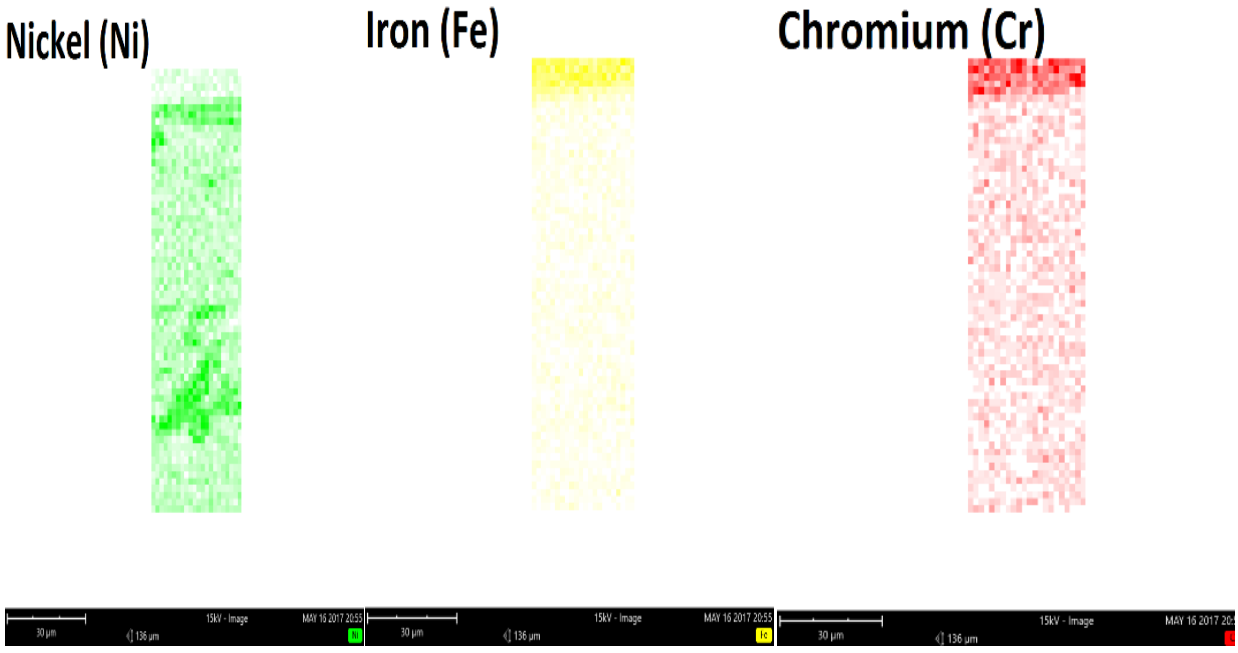
The results from EDS by using *Phenom Pro X* SEM for the elemental distribution along the Cu-SUS304 braze joint for the sample brazed at 650 ºC/15 min, are illustrated in Fig 1. It is evident in the EDS image (Fig 1) that the brazed joint primarily comprises of Cu-, Ni-, Sn- and P- rich phases. The EDS image is marked with seven points (1-7) within the marking area (dotted lines). Point (7) was marked inside the black-white dotted line boundary for mapping analysis purposes. There are six points (1-6) that were analyzed for the existence and concentration of elements. Points (2) and (5) represent the joint area of the filler metal interface with SUS304 and Cu, respectively. Points (3) and (4) represent filler metal that is close to the interfaces of SUS304 and Cu, respectively. Points (1) and (6) represent SUS304 and Cu, respectively that are next to the points (2) and (5), respectively. It is evident in Fig 1 that the filler metal section shows that the bright region indicates Cu-rich composition whereas the grey colored region indicates oxidized Cu with other elements such as Ni, Sn and P.

Figure 2 shows the average chemical analysis from the EDS for the different points (1-6) of the brazed joint. The point (1) corresponds to the chemical composition of SUS304 stainless steel. At this region, Fe-rich phases have been formed by combining with Cr or Ni.

The EDS results in Fig 2 reveal that Point (2) representing the composition of 304SS shows a little amount of Fe content on the reaction layer; however, the point 2 shows a high Ni contents. This elemental distribution leads us to a possible conclusion that Ni atoms from the filler metal diffused into SUS304 owing to the better solubility of Ni in Fe than that of Cu in Fe (Hume-Rothery rule of substitutional solid solubility) [10]. The low diffusivity and poor solubility of Cu result in minor copper content into this region [15].

The points (3) and (4), in Fig 2, represent the chemical composition of the filler alloy zone with varying concentrations of Fe, Cu, P, Ni and Sn; here, the low concentrations of Fe and Sn are worth noting. The poor solubility of Fe in Cu is the reason for the low Fe at.% in the filler alloy region. The reason for low Sn at. % might be attributed to the possibility of reaction of Sn with Fe and Cu to form an intermetallic compound: $FeSn_2$; this inference is in accordance with literature [16]. Additionally, some proportion of Sn atoms might have diffused from the filler metal into Cu (base metal) resulting in low at. % of Sn at point (4). The high at. % of Cu confirms that the filler metal is Cu-based. A look at Point (4) in Fig 2 indicates a low at.% of P in the filler metal; this elemental distribution may be explained as follow. Phosphorous (P) has the function of accelerating dissolution of copper during brazing and becomes the indispensable element in filler metals for brazing of copper; this explanation is in accordance with literature [17]. The points (5) and (6) are located at the Cu base; this is why there is a high at.% of Cu for these points in the EDS image (Fig 2).

Figure 3 illustrates the mapping analysis by use of SEM-EDS for a sample brazed at 660 ºC/15 min. Mapped SEM micrograph shows the brazed sample brazed; where the diffusion is likely to be associated with the separation of the filler metal and penetration depth of Ni and P to SUS304 and Cu. The sky-blue area is recognized as a Cu region that dominantly remained in the brazed area; whereas Fe (yellow) and Cr (red) slightly diffused in the brazed area (see Fig 3). The elemental distribution for the mapped SEM micrograph in Fig 3 is illustrated in Fig 4(a-f).



(a) **(b)** **(c)**

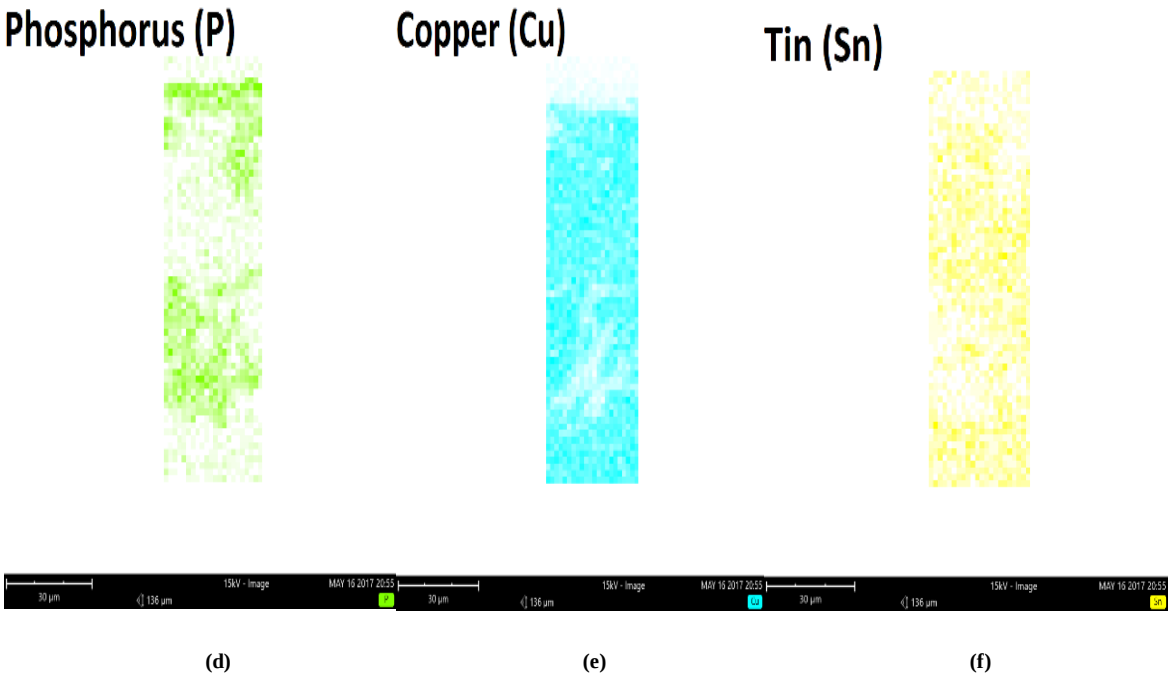


Fig 4. Element distribution maps showing the spatial distribution of each element in Fig 3; spatial distribution of: (a) Ni, (b) Fe, (c) Cr, (d) P, (e) Cu, (f) Sn

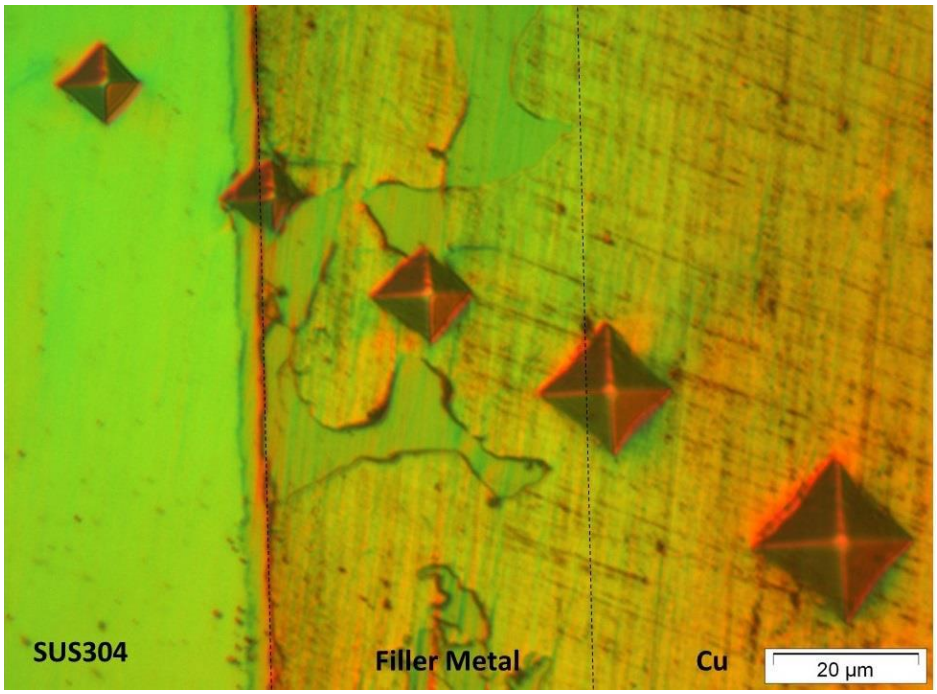


Fig 5. Microhardness indentation positions in a brazed sample

The elemental distribution/mapping analysis shown in Figs 3-4 can be explained on the basis of a possible brazing mechanism in the SUS304 SS-Cu braze joint, as follows. Firstly, the melting of Cu-based filler alloy started and a liquid metal zone was formed at the SUS304 SS/Cu interface. It continued with the diffusion of filler alloy to base metal and at the same time dissolution of base metal. This is why, the diffusion of a small amount of filler alloy is counteracted with the dissolution of a large amount of base metal and there is a significant relation between solid metal dissolution and liquid metal diffusion. When liquid filler alloy

contacts with base metal, the diffusion of filler alloy to base metal is governed by volume of liquid filler alloy and penetration of liquid filler alloy to base metal by grain boundary diffusion. This explanation is in agreement with literature [18].

B. Microhardness Analysis:

The microhardness of the brazed samples were measured at five different positions for each sample by applying a load of 10 kgf applied for a duration of 10 seconds; and then the average of each set of data was determined. The optical micrograph in Fig. 5 illustrates the five diamond indentations produced by a Vickers hardness micro-indenter; these indentations cover three regions: stainless steel (SUS304 SS), Cu-based filler metal (BFM: VZ2250), and copper (Cu) along with boundary line as a dotted line. The distance between the indentations was manually controlled by crossing the braze-joint area (< 40 μm^2). A typical sample brazed at 680 ^oC/15 min was considered for the micro-indentation in the Cu region; here, the arithmetic mean of the diagonal of diamond-shaped indentation was determined to be around 9 μm (d = 9 x 10^{-6} m = 0.009 mm). By taking F=10kgf, and d=0.009mm, and using Equation (2), an HV value of 22.8 kgf/mm^2 is obtained for a point in the Cu region for the sample brazed at 680^{o}C/15 min (see Fig 6).

Now we consider the overall microhardness data for all nine samples brazed at temperatures 640^{o}C, 660^{o}C, and 680^{o}C for time-durations of 5, 10, and 15 min. Figure 6 presents the graphical plot of the microhardness (HV) versus distance data for the nine brazed samples. It is evident in Fig 6 that the hardness values vary considerable depending on the brazing parameters. It can be observed that brazing at 680^{o}C/15 min results in the lowest microhardness (HV = 22.8 kgf/mm^2) in the Cu-brazed region. On the other hand, the highest hardness (HV = 140 kgf/mm^2) corresponds to brazing at 660^{o}C/10min in the SUS304 SS brazed region. In fact, the hardness of stainless steel at ambient temperature is higher (HV = 150-200) than as determined in the present study (HV=140); this reduction in hardness is scientifically justified owing to the softening effect on steel due to brazing temperature (thermal softening effect). There is also reduction in hardness on the boundary between the stainless steel and filler metal as compared to SUS304 SS.

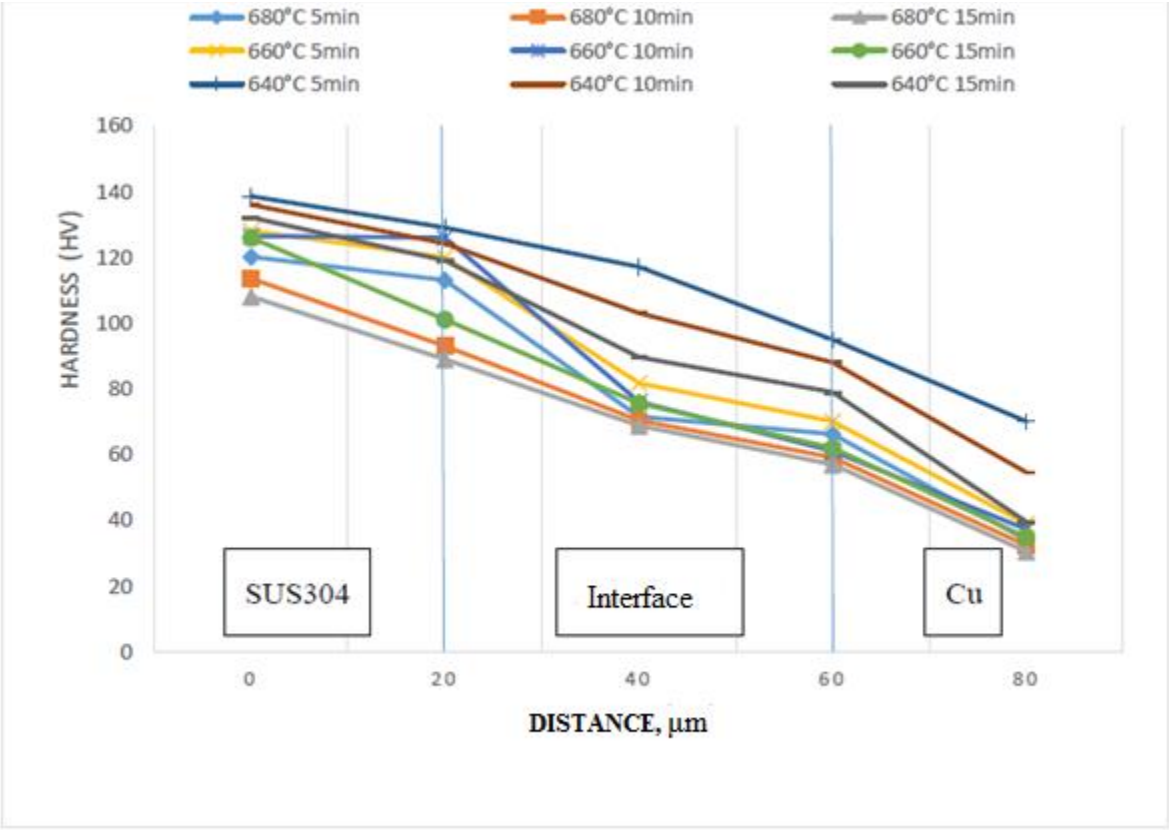


Fig 6. Microhardness (HV) versus distance graphical plot for the nine brazed samples
(Note: Vickers hardness, HV is expressed in kgf/mm^2 units)

A typical hardness value HV≅130 kgf/mm^2 at the interface of the braze joint can be noted for sample brazed at 660 ^{o}C/10 min (see Fig 6); this hardness value is encouraging and in agreement with the literature; which is justified as follows. Recently (2018), Beura and co-workers have reported an average microhardness HV≅100 at the interface of stainless steel/aluminum bronze brazed joint produced by using a silver-based BFM [19]; this hardness value is lower than the one reported in the present paper. Additionally, Rahman and co-workers (2016) have reported the highest recorded HV=125kgf/mm^2 in the filler metal region of a steel-*Al* braze joint [20]; this microhardness value is also lower than one (HV=130) at interface region of the braze joint, reported in the present study.

However, Jiang and co-workers have reported a considerably high micro-hardness HV ~ 250 for the braze joint [11]. This almost double the hardness value is neither discouraging nor surprising owing to the following two reasons: (a) Jiang and co-researchers have reported the hardness of the braze joint that was produced by using refractory metals (WC-15Co/35CrMo) that already have high hardness, and (b) Jiang and co-workers used silver-based BFM; which is very expensive as compared to the one reported in the present study. On comparing our hardness of braze joint (HV=130 kgf/mm^2) with that of a weld joint in an aluminum alloy (HV=90) as reported by Motlagh and co-workers (2012) [2], we find that our braze-joint hardness value is satisfactory because braze joints are usually weaker than weld joints. Hence, it is quite logical to conclude that brazing at 660 ºC/10 min results in a reasonably high hardness of 130 kgf/mm^2 at the braze joint.

CONCLUSION

It is concluded that a copper-based brazing filler metal (BFM: VZ2250) exhibits good brazing ability with an effective diffusion of the molten filler along the grain boundary; the latter was caused by the diffusion of iron (Fe) from stainless steel to filler metal. The EDS elemental distribution mapping analysis revealed that nickel (Ni) atoms from the filler metal diffused into SUS304 owing to the better solubility of Ni in Fe than that of Cu in Fe. This metallurgical behavior was found to be in accordance with Hume-Rothery rule for substitutional solid solubility. The chemical composition (at.%) of the filler alloy zone in the brazed joint showed low concentrations of Fe and Sn; the latter was justified by the possibility of reaction of Sn with Fe and Cu to form an intermetallic compound: $FeSn_2$. The average microhardness of samples brazed at 660ºC/10 min were determined to be around HV = 130 kgf/mm^2 in the filler metal region.

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