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RESEARCH

Development of Zn_{50} Brazing Alloy for Joining Mild Steel to Mild Steel (SAE1018)

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A B S T R A C T

This work has developed new brazing alloys for joining mild steel to mild steel (SAE1018) at a lower temperature. The alloys blends and error analysis were done by experimental design software (Design Expert 8.0.7.1). Design of experiments was done by Scheffe quadratic mixture method. The liquidus temperatures were predicted by calculation of phase diagrams of the alloying metals. The brazing alloys were produced by gravity technique and melted using silicon carbide graphite crucible. The quality of the brazing alloys was analyzed by optical microscopy (OM), atomic absorption spectroscopy (AAS) and fourier transform infrared spectroscopy (FT-IR). Brazed joints were produced by torch method with a commercial flux. Brazing temperatures (liquidus) were tracked by a digital infrared/laser pyrometer. Some mechanical properties studied were tensile strength and hardness. Finally, brazed joints produced from the developed brazing alloys were compared to that produced from muntz brass. Six (6) brazing alloys were successfully developed. Zinc and manganese were the main components, to which were added; 3 to 4 %wt silver and 11 to15 %wt modifying element. The microstructure showed a typical eutectic structure with zinc-rich phase distributed uniformly in the matrix with a combination of different sizes of dendrite, rounded blocks of compounds and hypoeutectic structures. AAS results indicated minimal out-gassing of zinc and FT-IR results indicated very low presence of atmospheric gas. The range of brazing temperature for best results was recorded from 690.90 to 735.10 ^{0}C. The joints produced from the developed brazing alloys had acceptable strengths with improved stress-strain behaviour compared to muntz brass.

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1. INTRODUCTION

Brazing had been useful in areas like artistic decoration, heating, ventilation, air-conditioning and refrigeration equipment, automotive, aerospace, construction and electronics. Its versatility allowed different assemblies to be joined together. Several brazing methods can be used based on the environment ranging from torch method in open air to vacuum furnace method. Torch and induction methods are most widely used by both artisans and industrialists. In any of the method employed, joints were fastened by means of brazing alloy with an appropriate flux where necessary.

Several brazing alloys had been developed based on the intended applications. One of the oldest brazing alloys developed is brass. The major filler in brass is copper with addition of 34 to 44 %wt zinc. Copper-zinc brazing alloy had liquidus temperature range of 870 to 903 ^{0}C. The liquidus temperature decreased as the added zinc increased. It was developed for brazing copper alloys and mild steel. The tensile strength of muntz brass (60Cu-40Zn) was found to be 620 MPa [1]. Brass had adequate tensile strength for the intended applications, but, its liquidus temperature was quite high for joining mild steel. That was because, the liquidus temperature of brass is within the annealing temperature range of mild steel (870 to 910 ^{0}C) and that had adverse effect on the chemical and physical properties of mild steel.

To tackle the shortcomings of brass filler, Cu-Mn-Ag and Cu-Mn-Ni-Sn were developed for brazing copper alloys and mild steel [2]. Their liquidus temperature ranges were found to be 830 to 880 ^{0}C and 750 to 850 ^{0}C for Cu-Mn-Ag and Cu-Mn-Ni-Sn respectively. Cu-Mn-Ag was reported to have tensile strength of 200MPa, and that of Cu-Mn-Ni-Sn to be 352 Mpa. The reduced liquidus temperature of Cu-Mn-Ni-Sn compared to Cu-Mn-Ag was attributed to the replacement of silver by alloys of nickel and tin in Cu-Mn-Ag. Tin was said to be temperature depressant in copper-based alloys [2]. Also, the poorer strength of Cu-Mn-Ag compared to Cu-Mn-Ni-Sn was attributed to presence of silver. Silver was known to reduce strength in copper-based alloys. The liquidus temperature ranges and tensile strengths of Cu-Mn-Ag and Cu-Mn-Ni-Sn were still not very favorable for mild steel applications. That was because, in brazing technology, the highest liquidus temperature has to be at least 50 ^{0}C lower compared to the lowest annealing temperature of the base metals for the base metal to retain its physical and chemical properties [3].

Another developed brazing alloy in commercial use was Ag-Cu-Zn. Silver was the major filler and it was developed for brazing copper alloys and mild steel [4]. The liquidus temperature range was 665 to 730 ^{0}C and it had tensile strength of 280 MPa. The liquidus temperature range was good for the intended applications, but, it had poor strength compared to mild steel which has tensile strength range of 410 to 750 MPa. The Ag-Cu-Zn filler was also not cost effective due to high cost of silver.

Further, to reduce the problems associated to Ag-Cu-Zn brazing alloys, Cu-Zn-Mn and Cu-Zn-Ni-Mn-Sn were developed for joining mild steel [5]. Their liquidus temperature ranges were found to be 799 to 930 ^{0}C. Their tensile strengths were also, reported to be of the range 270 to 285 MPa. Jacobson *et al,* (2002) used zinc as temperature depressant. It was found that the maximum amount of zinc that could be added was 46 %wt. More addition made the brazing alloys to be very volatile and brittle. That limited the amount of zinc that could be added and temperature reduction attainable. Cu-Zn-Mn and Cu-Zn-Ni-Mn-Sn have high liquidus temperature and poor tensile strengths for joining mild steel.

In the other hand, Mg-In-Zn was developed for brazing magnesium alloy AZ31B at 490 ^{0}C [6]. Mg-In-Zn had very good liquidus temperature, but, it was specifically developed for brazing magnesium alloy. Likewise, Cu-Sn-Mn-Ce was developed for brazing beryllium-copper assembly at 640 to 700 ^{0}C [7]. Both Mg-In-Zn and Cu-Sn-Mn-Ce which had good liquidus temperature were limited in applications and could not be used for joining mild steel.

A promising brazing alloy that was recently developed is Ag-Cu-Zn-Sn for joining copper alloys and mild steel at 750 to 790 ^{0}C [8]. It was reported to have tensile strength of 445 MPa. The tensile strength is adequate for the intended applications. However, the liquidus temperature is still appreciably high and it has silver as the major filler. Hence, it is not cost friendly.

In brazing alloys development, zinc was used mainly as temperature depressant and sometimes to aid wetting on the substrate [1,4-6,8]. It was also proved that with high chemical composition of zinc (≥46 %wt), the brazing alloys became very volatile and that limited the amount of zinc that could be added and temperature reduction attainable [5,9].

Sisamouth *et al*, (2010) in order to tackle the volatility of zinc investigated the gap filling ability of Ag-Cu-In brazing alloy on copper at temperature range of 677 to 770 ^{0}C. The silver content in that test was fixed at 60 %wt and indium was varied from 5 to 25 %wt. It was discovered that increase in indium led to decrease in the brazing temperature, but, showed no significant effect in the capillary rise height (that is non-improvement in wettability). Other properties of such materials may further be quantified using phase diagrams [10].

From literatures, the liquidus for joining mild steel were quite high compared to its annealing temperature range. There is need to reduce the liquidus temperature of brazing alloys for joining mild steel to retain its physical and chemical properties and also to save energy. Likewise, most of the reviewed developed fillers for joining mild steel had poor tensile strengths. Those that had adequate tensile strengths made excess use of silver or still have unfavorable liquidus temperature and need to be improved upon.

In review of abundance and material use, zinc is the 23rd most abundant element on earth. It was mined in more than fifty countries and 5th most used metal after iron, aluminium, copper and titanium [11]. Zinc is both more abundant and cheaper compared to copper and titanium. Renowned research had proved that zinc-based alloys are relatively cheap, can be processed efficiently with low energy consumption without endangering the environment and have combination of good properties [12]. Hence, its usage needs to be raised. Although, zinc based alloys showed decreased hardness and ultimate tensile strength in hybrid composites reinforced with groundnut shell ash, it had improved corrosion resistant in 3.5 % NaCl solution [13]. However, the excellent properties of zinc-based alloys have not been sufficiently harnessed in brazing technology [5]. It will be good in brazing alloy production due to its low energy requirement in processing.

Based on these findings, this study tends to develop Zn-based brazing alloys, employing experiments design, calculation of phase diagrams and other relevant scientific approach for joining mild steel to mild steel. The newly developed brazing alloys will have their liquidus temperature less than 750 ^{0}C with acceptable tensile strength. This study also tends to handle the high volatility and brittleness of zinc at appreciable temperature by addition of modifying and grain refining elements respectively. Finally, this study will characterize and analyze the brazed joints to reveal the amount of out-gassed components and inclusions during the brazing process.

2. MATERIALS AND METHODS

2.1 Candidates and base metal selection.

Candidates selected for the brazing alloy development were zinc, manganese and silver. These metals were reported to form solid solution and excellent mechanical mixture with each other and ferrous metal [5,14].

The base metal selected for the test was Bright Drawn Commercial Quality mild steel of Society for American Engineers specification (SAE 1018). That was chosen due to its wide applications in artistic decoration, machinery parts and automobile body building among others. Also, muntz brass was chosen as reference brazing alloy.

2.2 Development of design of experiment matrix.

The design matrix was developed by Design Expert 8.0.7.1, utilizing Scheffe quadratic mixture method. The Scheffe mixture method formed accounts for the natural constraints found in mixture models where the sum of all the components must equal to a constant or total. It did not have an intercept term as found in the slack form of mixture models and response surface methodology. The upper and lower limits of each component were coded. After several trial runs, the upper and lower limit coded values were determined as shown in Table 1.

The limit values of zinc, manganese, silver and modifying element were keyed and the possible alloys were generated by the program or read from the file as shown in Table 2. There were twenty experiment runs consisting of ten main, five replicated and five estimates of errors models.

Table 1. Iterated chemical composition limits of alloy components.

Comp.	Limits [%]		Equivalent values [%]	Mean [%]	Std
	Min.	Max.			
Zn	46.00	50.00	0.00=46.00 0.40=50.00	48.83	1.13
Mn	33.00	35.00	0.0=33.00 0.20=35.00	34.25	0.79
Ag	0.00	4.00	0.00=0.00 0.40=4.00	2.93	1.13
Mod.	11.00	15.00	0.00=11.00 0.40=15.00	13.98	1.15

Table 2. Design of experiments showing chemical compositions of alloys.

Experiment runs order	Zn [%]	Mn [%]	Ag [%]	Modifying element [%]
1	50.00	35.00	0.00	15.00
2	49.50	34.00	2.75	13.75
3	49.33	33.00	2.67	15.00
4	48.67	35.00	2.67	13.67
5	50.00	33.00	3.33	13.67
6	48.00	35.00	2.00	15.00
7	48.00	35.00	2.00	15.00
8	50.00	33.00	3.33	13.67
9	50.00	33.67	1.33	15.00
10	48.67	35.00	4.00	12.33
11	50.00	35.00	2.00	13.00
12	48.50	34.00	4.00	13.50
13	48.33	35.00	4.00	13.67
14	48.50	34.00	4.00	13.50
15	50.00	34.00	4.00	12.00
16	49.50	34.00	2.75	13.75
17	46.00	35.00	4.00	15.00
18	48.00	33.00	4.00	15.00
19	49.50	34.00	2.75	13.75
20	50.00	35.00	4.00	11.00

Errors were generated during blending of the mixtures. The values were estimated using Fraction of design space (FDS) graph. Figure 1 shows the FDS graph for the blend.

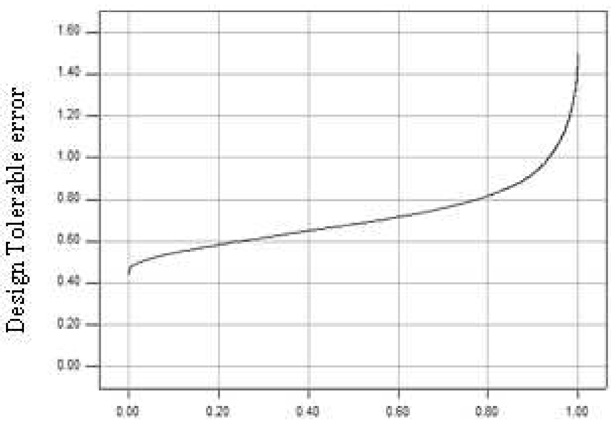

Fig.1. Fraction of design space graph.

The mean FDS curve is quite low and not steep. The minimum standard mean error is 0.44 and the maximum standard mean error is 1.5. These are quite good for the generated experiment runs in this study.

The tolerable components composition limits within the available design space were also estimated by mixture triangle FDS graph as shown in Fig. 2. It was discovered that the best blends occurred at component variation of 47.786 to 49.567 %wt zinc, 33.00 to 34.786 %wt manganese, and 1.784 to 3.567 %wt silver at a constant value of 13.857 %wt modifying element. This can be observed in Fig. 2, since, those ranges of component variation lies within the tolerable error contours limit.

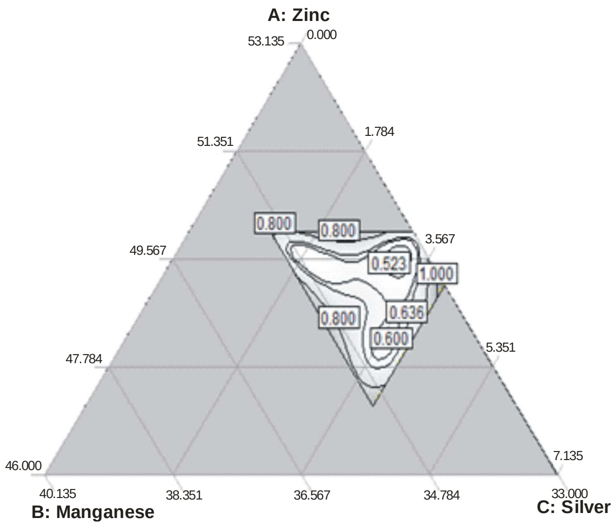

Fig. 2. Suggested components composition limits.

2.3 Conducting experiment from design matrix table.

Experiments were conducted from design matrix table. The procedures are presented in subsequent subsections 2.5 to 2.7.

2.4 Brazing alloy production

Brazing alloys were produced from design matrix table values using electrolytic zinc, manganese, silver and a modifier powder. For each mixture, the required amount of each element was calculated using the following equation:

$$A_i = 0.01E_d W \quad (1).$$

were;

A_i = amount of a component (g).

E_d = experiments run value of a component (%wt).

W = needed quantity of the alloy (g).

Equation (1) was arrived at following the percentage ratio conversion from the design of experiment matrix table. It was only applicable for production of specified quantity of the newly developed brazing alloy. The calculated values obtained in equation (1) for each component (Zn, Mn, Ag and the modifier) were measured using a digital scale. The measured quantities were mechanically mixed by gravity and centrifugal method (Electric motor 3000 rpm turning for 1 hour). A calculated quantity of flux was also measured and added/mixed with alloy by the same method. The required quantity of flux was calculated using the following relationship:

$$F = 0.8W \quad (2).$$

where;

F = quantity of flux (g).

Equation (2) was derived from wetting test carried out in this research. It is applicable only on the newly developed brazing alloy. Muntz brass wire of 1.0mm diameter was also procured for further test.

2.5 Brazing execution

The tensile strength, hardness and micrograph samples were prepared based on ASTM E8 standard. Brazing was carried out in an open air. Mild steel sheet of 110.00 mm length, 24.50 mm width and 1.70 mm thickness were prepared using snip cutter and grinding machine.

Two samples were placed end to end lapped and positioned on a galvanized steel sheet (4 mm) stage plate. The joint clearance was 0.29 mm based on mild steel to mild steel strength of joint recommendation [15].

The joint was slightly preheated (about 10 seconds). Then, the produced brazing alloy paste was placed on the preheated area. The arrangement was finally heated from room temperature (37.2 ^{0}C) to peak joining temperature for a time range within 64 and 80 seconds by a carbonizing flame of single oxy-acetylene torch. A pause of few seconds at 100 ^{0}C was observed to enable water in the brazing alloy and entrapped moisture from the environment to boil off. This is to prevent excessive spitting and frothing of flux. Wetting and filleting was observed by eye to have taken place around the joints. Other temperature dwells in the weld was deemed unnecessary. For each trial, an average heating rate of 10 ^{0}C/s was used. This average value was obtained from several heating trials. The brazed samples were cooled in still air.

The temperature dwells of all trials were tracked by digital Infrared/Laser Pyrometers (CEM dual laser-infrared & k-type thermometer, DT-8869) with capacity of –50 to 2500 ^{0}C. Three (3) to four (4) samples were produced from each alloy. Finally, three samples were produced using muntz brass filler metal (reference brazing alloy). A typical highlighted Zn-Mn-Ag brazed and tensile tested joint is shown in Figure 3. And, Figure 4 showed a typical brass brazed and tensile tested joint.

Fig. 3. Typical highlighted Zn-Mn-Ag brazed and tensile tested joint.

Fig. 4. Typical highlighted brass brazed and tensile tested joint.

It could be observed in Figs. 3 and 4 that failure occurred on the base material and not on the brazed joint. This is an indication of a good brazing alloy and brazing method used in this research work.

2.6 Properties Survey Test

Tensile test was done by computerized universal tensile testing machine, model number TUE-C-

100. The range is 100 KN with a cross head speed of 5 mm/s. The samples were at first fix in the chucks of the testing machine. The machine was then zeroed, balanced and calibrated and the conditions of the test were selected. Then, load was applied on the specimen until it breaks. The tensile strength was determined from the stress-strain diagrams. Also, the hardness measurement was done by universal hardness tester utilizing ball indenter at an applied load of 10 kg. The values obtained for different alloys are shown in Table 3.

Table 3. Determined mechanical properties.

Alloys	Liquidus (ºC)	Tensile (MPa)	Hardness (0.1Hv)
$Zn_{48}Mn_{35}Ag_{2}Mod_{15}$	665.21	290	220
$Zn_{48}Mn_{35}Ag_{4}Mod_{13}$	700.10	352	188
$Zn_{48}Mn_{34}Ag_{3.5}Mod_{14.5}$	694.31	340	195
$Zn_{50}Mn_{35}Ag_{4}Mod_{11}$	708.22	340	182
$Zn_{50}Mn_{33}Ag_{4}Mod_{13}$	690.18	405	187
$Zn_{49.5}Mn_{34.5}Ag_{3.5}Mod_{12.5}$	710.15	330	175
$Zn_{49.5}Mn_{34.5}Ag_{1.5}Mod_{14.5}$	710.15	330	175
$Zn_{49.5}Mn_{34.5}Ag_{1.5}Mod_{14.5}$	690.18	405	187
$Zn_{50}Mn_{35}Mod_{15}$	682.85	335	190
$Zn_{49}Mn_{33}Ag_{3}Mod_{15}$	720.80	500	194
$Zn_{47}Mn_{34}Ag_{4}Mod_{15}$	688.31	320	170
$Zn_{48}Mn_{34}Ag_{3.5}Mod_{14.5}$	724.11	488	189
$Zn_{49.5}Mn_{34.5}Ag_{3.5}Mod_{12.5}$	735.10	480	198
$Zn_{50}Mn_{33}Ag_{4}Mod_{13}$	724.11	488	189
$Zn_{50}Mn_{35}Ag_{2}Mod_{13}$	716.81	510	180
$Zn_{46}Mn_{35}Ag_{4}Mod_{15}$	700.10	352	188
$Zn_{48.667}Mn_{35}Ag_{2.667}Mod_{13.667}$	750.70	350	200
$Zn_{48}Mn_{35}Ag_{2}Mod_{15}$	719.33	380	190
$Zn_{48}Mn_{33}Ag_{4}Mod_{15}$	700.10	352	188
$Zn_{50}Mn_{33}Ag_{2}Mod_{15}$	718.36	512	180

Further, the morphology observation was examined by optical microscopy (OM, OLYMPUS GX51 Scanning electron microscope). A solution of 90 % ethanol and 10 % nitric acid was used for etching.

As well, the fillets were analyzed by Fourier transform infrared spectroscopy (FT-IR, Buck 530). Finally, fillets chemical composition (metallic) characterization of the developed brazing alloys was done by Atomic absorption spectrometer (AAS, Agilent 240 FS AA) with air-acetylene flame and hollow cathode lamp of current 4-5 ηA (double ray). Digestions of samples were done by a muffle furnace.

2.7 Phase Diagrams Calculations.

Thermodynamic calculations of the phase diagram examined were performed using CALPHAD of ThermoCalc 5.0 software [16]. It was done to estimate the solubility limit of the solutes in the solvent, the activation temperatures and liquidus temperature of the alloying elements at certain components composition. The phase diagrams also helped to predict the formation of brittle intermetallic compounds known as sigma (δ) phase. Among the binary phase diagrams that were examined are Zn-Ag and Zn-Fe. Hence, feasible limits of components were chosen in such a way that the alloys were free from visible defect and had all features that enhanced mechanical properties.

At a pressure of 1 atmosphere, typical binary phase diagrams calculated in this study are shown in Figs. 5 and 6.

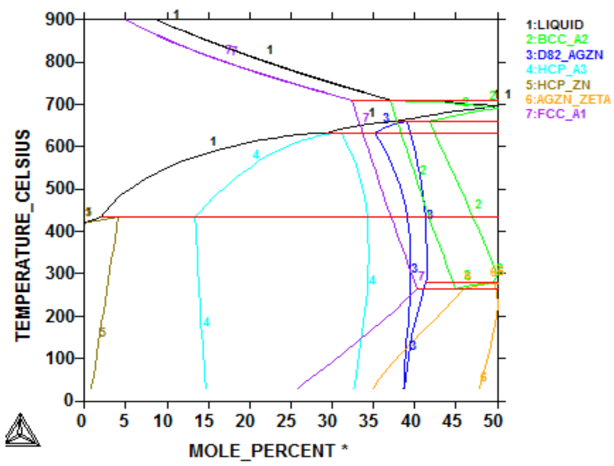

Fig. 5. Zn-Ag binary phase calculations.

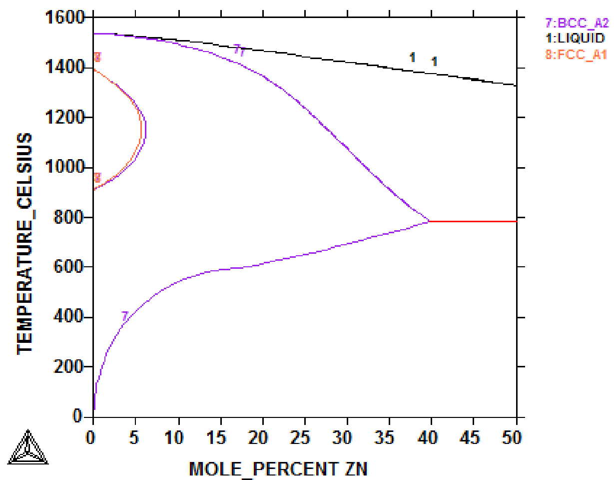

Fig. 6. Zn-Fe binary phase calculations.

In the Zn-Ag phase equilibrium systems (Fig. 5), seven different phases could be seen. These include silver-rich phase (α-phase or FCC_A1 between line 7 and right side of temperature axis), the zinc-rich phase (η-phase or HCP_Zn as given by between line 5 and left side of temperature axis), β-phase (BCC_A2 given by inside portion of line 2), ζ-phase (AGZN_ ZETA as shown by inside portion of line 6), ɣ-phase ($D8_2$_AgZn as given by inside portion of line 3) and ε-phase (HCP_A3 as given by inside portion of line 4).

The percentage composition of zinc in the α-phase region is between 0 and 40 percent weight. It has flow temperature of 709.74 ^{0}C and stable to temperature of melting point of pure silver as indicated by portion above line 1. The next phase after α-phase is the ζ-phase. This is a stable low temperature phase near equi-atomic compositions. ζ-phase unit cell contains nine atoms, three of the positions are occupied almost exclusively by zinc and the remaining six positions are occupied at random by the remaining atoms (75 % silver and 25 % Zinc). Accordingly, the sub-lattice model proposed was $(Zn)_3(AgZn)_6$. The ζ-phase is designated as AGZN_ZETA and the zinc chemical composition is between 37-51.2 %. It had reaction temperature between room and 261.96 ^{0}C. Likewise, β-phase is an ideal composition of silver and zinc. It had high stable temperature. The maximum reaction temperature of β-phase was 660.11 ^{0}C and the zinc composition is between 36.7 and 58.6 %.

The chemical composition of zinc in ɣ-phase is between 58.5 and 64.7 percent. The ε- phase is a zinc-rich phase with chemical composition between 66.2 and 89 % Zinc and maximum reaction temperature was 630.37 ^{0}C. The η-phase is a zinc-rich phase with chemical composition of 95 to 100 % Zinc and had maximum reaction temperature of pure Zinc. Hence, at a temperature of 709.74 ^{0}C, complete wetting must have taken place for Zn-Ag binary phase. Also, there is no evidence of formation of sigma-phase which was reported to induce brittleness [4].

In similar calculations, complete wetting was expected to have taken place in Zn-Mn phase at a liquidus temperature of 750 ^{0}C and at lower liquidus compared to Zn-Ag binary phase in Zn-Mn-Ag ternary phase. The implication of these temperatures is that for complete wetting of the alloys, it must be heated to at least the minimum liquidus temperature of a phase that has the highest reaction temperature. Also, between the temperatures, there will be eutectic and hypoeutectic structures.

The estimated liquidus temperature range of the developed brazing alloys by calculation of phase diagrams was of the range 650 to 750 ^{0}C. Also, the fusion temperature within the brazing alloys and into the base metal was of the range 280 ^{0}C to790 ^{0}C as shown in Figs. 5 and 6.

3. RESULTS AND DISCUSSIONS

3.1 Effect of zinc on liquidus temperature.

In the Scheffe mixture models method, the effect of a component in the mixture on a mechanical property is relative. This is because, as one component increases, one or more other component must decrease. The sum of the components must equal to a constant at any instant. Therefore, the effect of zinc in the newly developed zinc-based brazing alloys on its liquidus temperature was studied using mixture triangle. First, two components were varied keeping the remaining two constant. Secondly, three components were varied and one kept constant. The effects of two components variation on liquidus temperature are shown in Fig. 7.

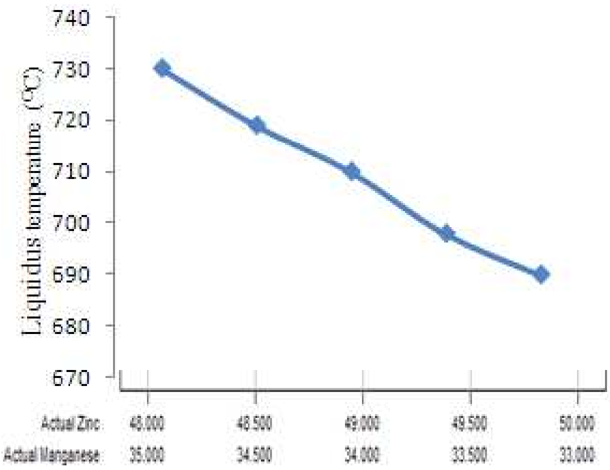

Fig. 7. Effect of zinc with manganese on liquidus.

At constant values of silver and the modifying element, increase in zinc with corresponding decrease in manganese continuously decreases the liquidus temperature of the alloys as shown in Fig. 7. The approximate minimum liquidus temperature attained at maximum zinc and minimum manganese addition is 684O C. But, the approximate maximum liquidus temperature attained at minimum zinc and maximum manganese addition is 720O C.

At constant values of manganese and modifier, increase in zinc with corresponding decrease in silver sharply decreases the liquidus temperature of the alloys. The approximate minimum liquidus temperature attained at maximum zinc and minimum silver addition is 684O C. But, the approximate maximum liquidus temperature attained at minimum zinc and maximum silver addition is higher compared to maximum manganese addition at constant silver.

Similar result was obtained in constant values of manganese and silver. But, it has less maximum liquidus temperature. This less energy requirement is attributed to the function of the modifying element which reduces volatility of zinc. Hence, the modifying element absorbed much of the energy that would have escalated volatility of zinc.

Further, the effect of variation of three components and one component kept constant on liquidus temperature of the brazing alloys are shown in Fig. 9. These contours were plotted at maximum composition of the constant components.

At maximum composition of the modifying element (15.00 %wt), it was discovered that the major component that raised the energy requirement of the brazing alloys is silver as clearly indicated in Fig. 8.

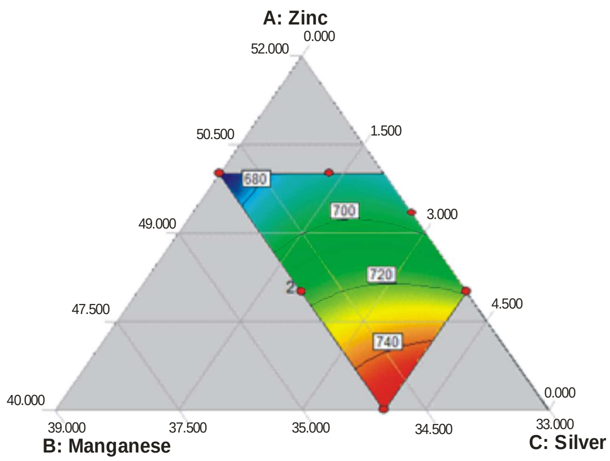

Fig. 8. Effect of zinc with silver and manganese on liquidus temperature.

However, increase in manganese slightly raised the energy requirement of the brazing alloys. But, zinc is the major energy absorber. The maximum liquidus temperature obtained at maximum composition of the modifying element is 740O C. This maximum liquidus temperature was obtained at maximum and minimum composition of silver and zinc respectively.

The minimum liquidus temperature was obtained at maximum and minimum composition of zinc and silver respectively.

Therefore, it could be concluded that addition of zinc reduced the energy requirement of the alloys as clearly indicated in Figs. 7 and 8. This effect of liquidus temperature reduction by zinc addition is in correlation to brazing alloy developments findings, where; zinc was mainly used as temperature depressant [1,5,6,8,17].

3.2 Effect of silver on tensile strength

It was observed that silver had dominant effect on the tensile strength of the newly developed brazing alloys as indicated in Fig. 9.

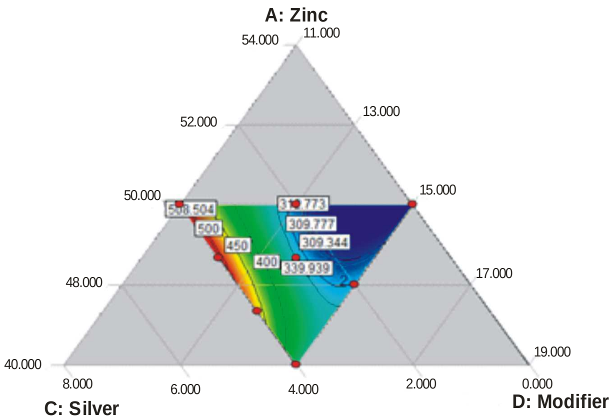

Fig.9. Effect of zinc with silver and modifier on tensile strength.

It could also be inferred that addition of silver increases the tensile strength of zinc-based brazing alloys. This effect of tensile strength enhancement of zinc-based alloy by addition of silver is in tandem with literature [18].

3.3 Effect of alloy components on vickers hardness

The effect of variation of any of the three components keeping any one of them constant was noticed to be distributive. There is none of the components that were observed to have good control over the hardness of the alloys. However, manganese seemed to have predominant effect on the hardness of the brazing alloys as indicated in Fig. 10.

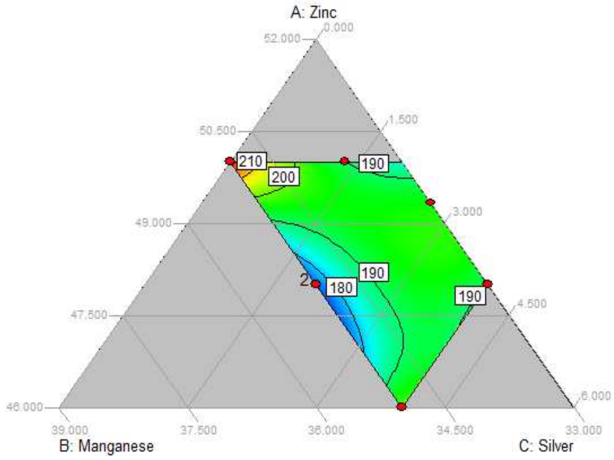

Fig. 10. Effect of zinc with manganese and silver on vickers hardness.

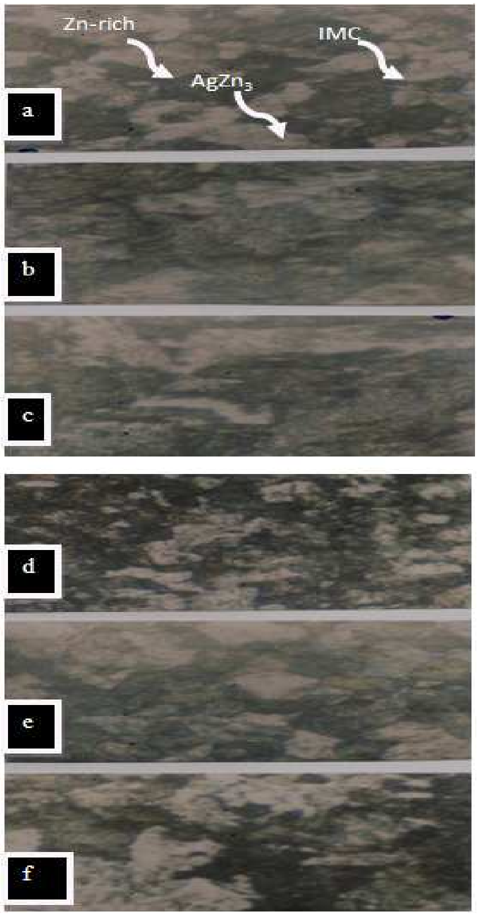

Fig. 11. Microstructure of six (6) different Zn-Mn-Ag brazing alloys.

Metallographic studies showed that the grain structures of Zn-Mn alloy could be refined by addition of silver. It was believed that the addition of silver in the Zn-Mn alloy destroys the uniform eutectic structure and leads to formation of silver compound, a hypoeutectic matrix that resulted to enhanced tensile strength. The OM of the developed brazing alloy has a good refinement which is an indication of an excellent solid solution and mechanical mixtures of the components as shown in Fig. 11. Figure 11b had best microstructure refinement. That could be as a result of relatively less zinc composition compared to other examined experiment runs at the same added quantity of silver.

As shown in Fig. 11, the microstructure of the Zn-Mn-Ag alloys showed typical eutectic structures with zinc-rich phase distributed uniformly in the matrix. The variation in percentage composition of silver, manganese and modifying element in the developed alloys resulted in combination of different sizes of dendrite, rounded blocks of other compounds and hypoeutectic structures. Decrease in zinc and keeping silver constant increases the formation of the dendrite and rounded blocks compounds as indicated in experiment 11b and 11f. That could be as a result of the role of silver in microstructure refining as reported in zinc alloy production [18]. Further, Increase in liquidus temperature was reported to enhance formation of brittle intermetallic compounds as reported by the study of Ag-Zn system [19].

3.4 The Fillets Inclusions

The FT-IR bands are considerably narrow in shape and combination of reasonably strong, medium and weak bands. The above characteristic bands is as a result of presence of larger crystal sizes of the metallic particles in the developed brazing alloys compared to the size of active organic elements which were known to have broader shape spectra. There is evidently the weakest band signal of 3695.6 cm^{-1} as shown in Fig. 12. That was attributed to very low hydrogen or hydroxyl functional group entrapment during the brazing or alloying process. The low hydrogen entrapment was attributed to flux shielding. Other bands noted within the hydroxyl functional groups region are evident at 3551.4, 3342.5 (with shoulder at 3500), 3174, 3035.3, 2882 and 2710.7 cm^{-1}. The absorbance increases with decrease in frequencies within the hydroxyl functional group range. The increase in band signal as the frequency decrease is a function of temperature.

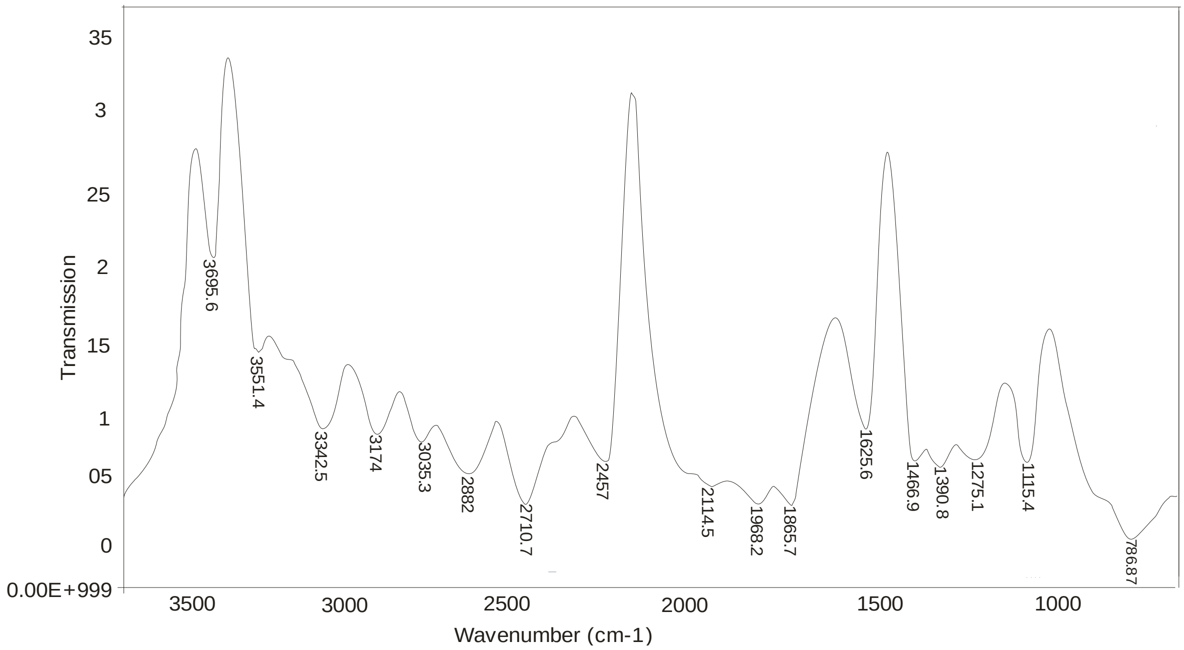

Fig. 12. Typical spectrums of the newly developed Zn-Mn-Ag brazing alloys.

Table 4. AAS result of ten (10) zinc-based developed brazing alloys.

Alloys number	Components concentrations(%wt)						
	Zinc	Manganese	Silver	Modifier	Iron	Other components	Out-gassed zinc
2	48.84	33.97	2.73	13.74	0.003	0.067	0.66
5	49.25	33.00	3.33	13.67	0.001	3.532	0.75
9	49.59	33.27	1.33	15.00	0.0009	0.399	0.41
10	47.67	33.89	3.81	12.33	0.010	1.290	1.00
12	47.69	33.91	3.83	13.50	0.016	0.244	0.81
13	47.62	33.94	3.85	13.67	0.027	4.033	0.71
15	48.80	33.92	3.83	12.00	0.006	0.144	1.20
17	45.88	34.99	3.97	15.00	0.035	0.005	0.12
18	47.78	32.98	3.96	15.00	0.009	0.051	0.22
20	47.90	34.90	3.80	11.00	0.008	0.292	2.10

The bands at frequencies 2114.5, 1968.2, 1865.7 and 1625.6cm^{-1} are related to species CO-Zn^{+2}, CO-Mn^{+2}, Ag^{+1}-CO-Ag^{+1} which occurred due to lack of pre-reduction in the production process and also due to coalescence of other metal particles. The bands at lower frequencies are evident at 1466.9, 1390.8, 1275.1, 1115.4 and 786.7cm^{-1} with shoulder at approximately 900cm^{-1}. Those bands were attributed to the stretching vibrations of P═O, P─O─C, C─C, C─C and C─N functional groups. That was as a result of release of some elemental phosphorus and carbon from the base metal and entrapment of some elemental oxygen and nitrogen from the atmosphere during brazing or alloying process. These undesired elements were insignificant as indicated by the AAS result in Table 4.

Therefore, it could be concluded that the spectra of the newly developed brazing alloys indicated low presence of atmospheric associated functional group elements and very high presence of metallic associated functional group elements. These were attributed to good shielding against atmospheric gases by Sifbronze flux used in this study.

3.5 Effect of Modifying Element on Volatility of Zinc

There is little decrease in chemical composition in each element compared to the calculated amount in production of the newly developed brazing alloy as shown in Table 4. Zinc variation is from 0.12 to 2.10 %wt. The excellent correlation between the design of experiment values and AAS determined values proved that there was little out-gassed zinc which was predominant at significant addition of it in brazing alloy development [5]. The out-gassed zinc decreases with increase in modifying element as shown in Fig. 13. It could be concluded that the added modifying element used in this study reduced out-gassing of zinc which was reported in zinc-based brazing alloy at appreciably high temperature [5].

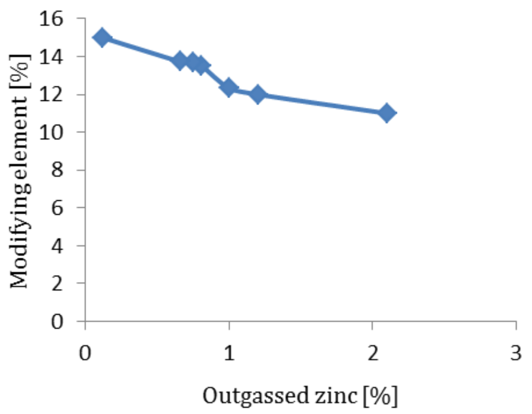

Fig. 13. Effect of modifying on volatility of zinc.

There were traces of Iron in the brazed joint beads. The iron inclusion increases with increase in temperature as shown in Fig. 14. This inclusion was believed to be due to partial alloying of brazed joint bead with the base metal. The inclusion is from 0.0009 to 0.0352 %wt.

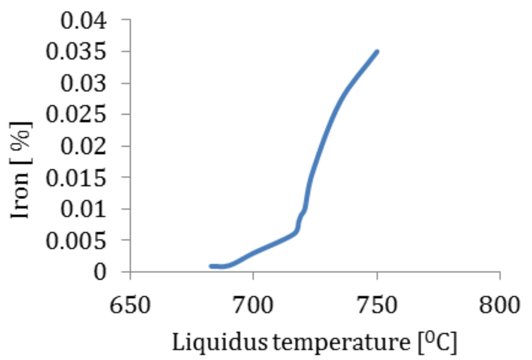

Fig. 14. Effect of liquidus temperature on iron inclusion.

Other inclusions were suspected. That was because the total alloy composition did not add up to 100 %wt. The range of other inclusions in the examined design of experiment runs was from 0.005 to 4.033 %wt. The low mean inclusion which is approximately 1.006 %wt indicated an excellent activeness of the sifbronze flux, addition of modifying element and low liquidus temperature used in this study.

3.6 Comparison of Brazed Joints

Six brazed joints of the developed brazing alloys were compared to muntz brass brazed joint. The correlated stress-strain curves are shown in Fig. 15. The pattern of the stress-strain curves for all samples are similar. However, zinc-manganese-silver brazed joints have higher stress at yield compared to that of muntz brass filler. In the other hand, muntz brass filler has higher strain at peak stress compared to that of zinc-manganese-silver filler.

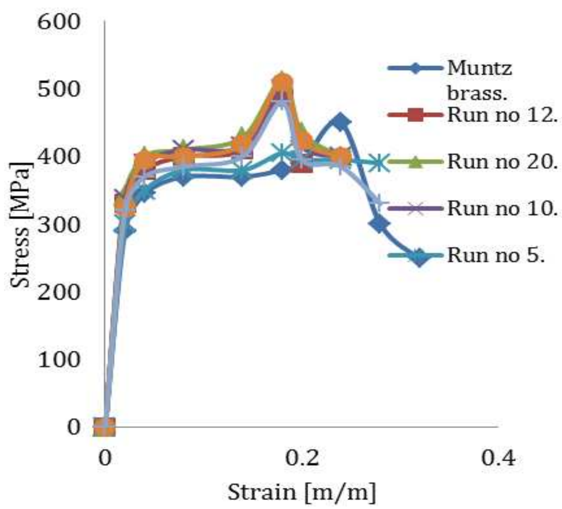

Fig. 15. Stress-strain curves of new and reference brazing alloys.

It can be deduced that zinc-manganese-silver brazed joints produced less ductile base metal compared to muntz brass filler. And, zinc-manganese-silver produced adequate elongation for the intended application. It can also be seen that zinc-manganese-silver brazed joints are capable of absorbing more loads before failure compared to base material brazed with muntz brass, which is similar to ductile material characteristics.

Finally, it can be concluded that zinc-manganese-silver brazing alloys with addition of modifying element produced better joints compared to muntz brass, which could be due to reduced liquidus temperature of the former.

4. CONCLUSION AND RECOMMENDATIONS

4.1 Conclusion

It could be inferred that brazing alloys of chemical composition up to 50 %wt of zinc developed was successfully utilized to produce an acceptable joint.

The developed Zn-Mn-Ag brazing alloy with modifying element required less energy and produced better joint compared to muntz brass in joining mild steel to mild steel.

It could also be seen that; addition of silver up to 4.00 %wt enhances the tensile strength of the developed Zn-Mn-Ag brazing alloys.

It was as well discovered that addition of modifying element minimized volatility of zinc.

Sifbronze flux (mixture of boron and boric acid) with Zn-Mn-Ag brazing alloy is good in Torch brazing (oxyacetylene) for joining mild steel to mild steel.

4.2 Recommendations

It is recommended that further research should be conducted in development of zinc-based brazing alloys to substitute silver by another cheaper element that can further reduce its liquidus temperature, produce acceptable joints and handle zinc's volatility.

Also, it is recommended that the wetting ability of zinc-based brazing alloys should be examined by other fluxes and substrates other than sifbronze and mild steel respectively.

Further, it is recommended that the zinc-based brazing alloys should be tried to join other metals other than mild steel.

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