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Possibility of Al-Si Brazing Alloys for Industrial Microjoining Applications

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Abstract: Aluminium alloys have been used widely since hundreds of years in automotive joining. Silicon is an excellent alloying element that increases the fluidity, depresses the melting temperature and prevents shrinkage defects during solidification, and is cost effective raw material. In recent few decades, research on cast Al–Si alloys has been expanding globally in military, automobile and aerospace industries. These alloys are good wear and corrosion resistant which depends on processing parameters and service conditions. However, the formation of big Si-needles in Al-Si alloys is a serious issue in joining industries. Silicon modification treatments are generally carried out to improve their durability and strength. This paper covers an elaborative study of various Al-Si alloys, the modification strategies to refine the Si-needles, effect of processing parameters and joining characteristics for automotive applications.

Keywords: Al alloys, Brazing, Welding, Silicon, Casting, Automotive

1. Introduction

1.1. Alloy

An alloy can be defined as a material having metallic properties as a result of a combination of two or more elements where at least one element is a metal. The metal atoms are predominant in chemical composition and the metallic bonding.[1-2] In general, the alloys have a wide range of properties different from the individual elements. Alloy is generally synthesized by mixing one or more metals or nonmetals at an atomic scale to enhance the various thermodynamic and mechanical properties. As a simple example, the alloy of Fe and C is steel, which is stronger than each of Fe and C primary elements. The physical properties of these alloys, like density and conductivity, may or may not differ greatly from the individual components. However, there are certain advanced engineering characteristics, e.g., tensile strength, shear strength, toughness etc., may be reasonably improved from those of the individual elements .[3-4]

1.2. Al Alloys

In recent few decades, the aluminium alloys have been used widely in automotive, automobiles, and aerospace industries. Aluminium is the materials of choice for various transportation and structural materials and is a cheaper alternative to steel in few of the cases. For instance, aluminium alloys containing the additives, Mg and Si, are now being replaces with steel panels in automobiles. This is particularly true in view of their excellent and attractive properties, light weight, less fuel consumption, and ease of transportation. Various elements are available for alloying in aluminium matrix, most commonly used ones are Cu, Mn, Mg, Si, Zn, etc. In outer atmosphere, aluminium forms an inherent surface layer of aluminium oxide which protects it for external environmental damage. Due to these factors, aluminium alloys were the important subject of research in the past few decades.[3-4]

1.3. Nomenclature of Aluminium Alloys

Aluminium alloys have been divided into various categories depending up to the major alloying element. The designations have been devised by the Aluminium Association Wrought Alloy Designation System. The nomenclature system consists of four numerical digits as shown in Table 1.[3)]

1.4. Characteristics of Al Alloys

Aluminium alloys covers a wide set of mechanical, physical, electrical and thermal properties which are improved upon the pure aluminium metal. The important properties include:

(1) Density: Aluminium is a light weight metal with a density of about 2.7 g/cm^3. If we compare with steel, aluminum has approximately 1/3 of the density of the steel.

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Table 1. Nomenclature of Al Alloys and Applications[3)]

Alloy Series	Major Alloying Element	Uses
1XXX	Nil (High Purity Al)	Electrical Conductors, Chemical Processing
2XXX	Cu	Aerospace, Automotive
3XXX	Mn	Architecture
4XXX	Si	Brazing, Automobiles, Heat Exchangers
5XXX	Mg	Submarines, Ships
6XXX	Mg, Si	Architectural Extrusions
7XXX	Zn	Aircrafts
8XXX	Others (Fe, Ti, Ni etc.)	
9XXX	Not Assigned	

(2) Oxidation resistance: As already discussed, aluminium contains an inherent oxidized layer of alumina over its surface that prevents it from the progressive oxidation and corrosion attack when exposed to air.

(3) Electrical and thermal properties: Aluminium alloys are highly electrically and thermally conductive. For example, the thermal conductivity of aluminium is approximately twice to that of copper of similar weight of both elements.

1.5. Al-Si Alloy

Al-Si alloys have a special class among all aluminium alloys. Their importance in various multidimensional industries lies in the fact that they exhibit high strength/weight ratio, excellent wear and oxidation resistance, low density and coefficient of thermal expansion (CTE) etc. Alloying aluminium with silicon improves the fluidity and reduces the shrinkage levels during solidification and processing which improves the weldability and castability. The silicon in Al-Si alloy plays an important role in depressing melting point and improving strength. Silicon has a density of around (2.34 g/cm^3) which further reduces the weight of the resultant cast alloy component. The poor solubility of Si in Al causes it to segregate out as a residual hard Si phase and improve the tribological properties.[5)] The eutectic point in Al-Si system is found near 12.6 wt% silicon having a melting point of ≈577°C. The eutectic Al-Si alloy designates the special and important composition with a minimum possible melting point of Al-Si alloys as per the phase diagram.[2-3, 4-5)]

As noted from the Table 1, the Al-Si alloys are marked as 4XXX alloys as per the Aluminium Association Wrought Alloy Designation System. The main characteristics of the 4XXX series aluminium alloys are:[3)]

(1) Heat treatable

(2) Excellent fluidity and strength

(3) Compatible to joining by brazing and soldering processes.

1.6. Applications of Al-Si Alloys

(1) In vehicles body parts, trains, structural parts, body structure and air conditioning. Cast Al alloys have been in use in various automobile bodies for a long time. In vehicle engines, the heavy engine blocks are now made from cast iron to aluminium alloys for weight reduction. Aluminium castings are almost used for making pistons, piston heads, axle, housings, and shafts etc. Al alloy castings are also used for wheels, brackets, brakes, suspension supports, air bag, shafts, knuckles, housings, instrument panels, etc. Al alloys have also been used mostly in heat exchangers for joining, especially Al-Si alloys. Al-Si is used generally for many automotive joining and body parts, e.g., pistons, cylindrical linings, etc.[6)]

(2) As already discussed, Al-Si alloys are the most diversified foundry alloys for engine pistons in automotive. However, the hypereutectic alloys are limited in use at commercial scale because of the difficulty in casting and machining due to the high Si percentages. Addition of high percentages of Si in Al, also increases the amount of heat capacity removed dissipated from the alloy for solidifying in casting operations.[7)]

2. Phase Diagram

Al-Si alloy is fundamental binary eutectic phase diagram with limited solubility of Al in Si and limited solubility of Si in Al. The only invariant reaction in Al-Si phase diagram is given by:

$$L \rightarrow \alpha + \beta \text{ (eutectic)}$$

Here, the liquid phase is L, The α-phase is primarily Al, and β is mainly Si. It is now widely recognized that the eutectic point is around ≈577°C at 12.6% Si. Aluminium silicon alloys are the casting alloys which are most used in foundry for the

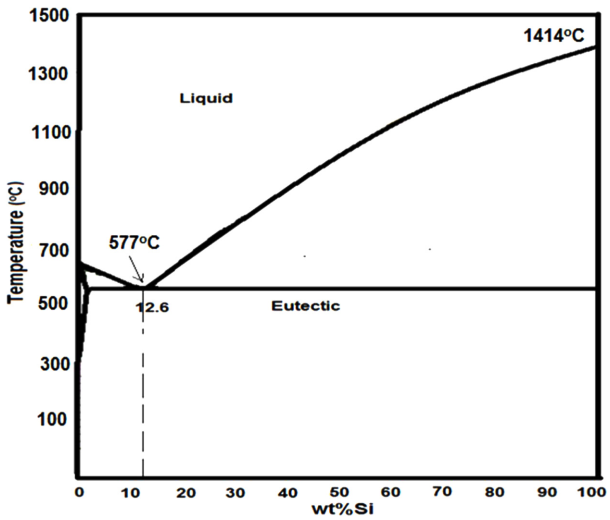

Fig. 1. Al-Si binary phase diagram.[8)]

fabrication of piston in automotive engines.[3-4, 6-7)] The Al-Si alloys can be categorized into three major categories:

(1) Hypoeutectic (<12.6 wt% Si),

(2) Eutectic (≈12.6 wt%Si), and

(3) Hypereutectic alloys (>12.6%Si, especially 17-23 wt %Si).

3. Modification in Al-Si Alloys

The variation in silicon shape, size, and structure in Al-Si alloy can be found in between different sections of cast structure. This affects the mechanical properties of the Al-Si specimens drastically and fail the joint. This problem becomes severe when applied to the brazing industries for joining applications. Primary Si, therefore, must be modified by using a number of approaches in the literature for a better and improved wear and friction resistance. All these mentioned reasons prohibit the use of hypereutectic Al-Si alloys over hypoeutectic Al-Si alloys. On the contrary, the use of hypoeutectic and eutectic Al-Si alloys is widespread due to their efficient method of production in the absence of big Si needles, good control of process parameters, and easier machinability. However, most of them are not suitable for high-temperature applications, as the tensile strength diminishes at elevated temperatures. Therefore, modification of Si, for hyper-eutectic Al-Si alloys, is necessary for uniform properties and high stability of the alloy.[9-12)]

3.1. Microstructural Modification by Grain Refiners, Inoculants, and Nucleating Agents

Hypoeutectic Al-Si alloys have a higher amount of α-Al in their microstructure. Unmodified Al–Si alloy has big, hard and brittle flakes of silicon that results in brittle failure during operation. To prevent this modifiers are added to Al-Si alloys to modify the Si particles from big needles/plates to fine round shape. As a consequence, the mechanical properties of the Al-Si alloys is greatly improved. Grain refiners have been tried to refine the α-Al grains thereby causing the grain refinement of α-Al phase in the form of a columnar grain structure after solidification. Various kinds of Al-Ti master alloys, e.g., Al-Ti-B alloys have been tried as a grain refiners in the past for Al-Si alloys.[9)]

The mechanism of grain refinement can be well understood by the nucleation and growth process of Al grains. Theoretically, the process involves both the homogeneous and heterogeneous nucleation. At industrial level, the wrought and cast aluminium alloys are generally grain refined before actual casting. Various commercial nucleating agents are also commonly used. For example, inoculating agents are often added in the aluminium melt during casting. In last few decades, there have been many investigations to avoid or stop the grain growth of the aluminium melts, e.g., Al-Ti, Al-B, Al-Ti-C, Al-Ti-B, and Al-Sr-B alloys.[9, 13-14)] The commercially available grain refining agents are summarized in Table 2.

Table 2. Common Grain Refiners in Al-Si Alloys.[14)]

Alloy	Composition
Al-Ti	Al-10Ti
	Al-6Ti
Al-Ti-B	Al-3Ti-1B
	Al-5Ti-0.6B
	Al-3Ti-0.2B
	Al-5Ti-0.2B
	Al-10Ti-0.4B
	Al-1.6Ti-1.4B
	Al-1.2Ti-0.5B
	Al-3Ti-3B
	Al-1Ti-3B
Al-B	Al-10B
	Al-5B
	Al-3B
Al-Sr-B	Al-10Sr-2B
Al-Sr-Ti-B	Al-10Sr-1.6Ti-1.4B
Al-Ti-C	Al-6Ti-0.02C
	Al-3Ti-0.15C
Al-Sc	Al-1Sc
	Al-2Sc
Mg-Zr	Mg-25Zr
	Mg-33.3Zr

3.2. Microstructural Modification by Friction Stir Processing

Various methods like friction stir processing (FSP) approach has been tested by few researchers for Si modification. According to the investigation carried out by Sima Ahmad et al.,[15)] while working on A356 alloy consisting of primary α-Al dendrites and inter dendritic irregular Al–Si eutectic regions, the use of FSP resulted in a significant modification of the big and large Si needles and Al-dendrites, thereby creating a uniform distribution of fine and spherical Si particles in the Al-Si matrix. The authors explained this behavior related to the intense plastic deformation at high friction temperature during FSP that gave rise to the development of the fine and equiaxed dynamic recrystallized grains.[15)] It was also reported that the an increase in the rotation rate resulted in an decrease of Si size and aspect ratio as well as the porosity level also found to reduce due to the severe stirring effect.

3.3. Microstructural Modification by Nanoparticles

In recent few years, there has been an enormous research activities on refinement of intermetallic compounds by use of nanoparticles.[16-24)] In Al alloys, various efforts have been paid to refine the Si needles as well the $CuAl_2$ phases by nanocomposite approach.[25-26)] The various kinds of nanoparticles are used to refine the Al grain size, Si needles as well the $CuAl_2$ intermetallic in Al-Si-Cu alloys. Sharma et al. have published recently a number of research results where they have used ZrO_2, SiC, La_2O_3 to refine the Si needles and intermetallic compounds in Al-Si-Cu alloys.[27-32)]

4. Brazing characteristics of various Al-Si alloys

The brazing of Al alloys involves a number of steps according to the joint material. Prior to brazing, the joint surfaces should be cleaned to have sufficient wettability and to prevent the buildup of defects in the brazed joints. The various types of pre-requisites are as follows:

1. Surface cleaning
2. Optimum clearance and fit
3. Application of flux of good quality (NOCOLOK etc.)
4. Proper fixation of the two parts
5. Application of heat to the joint
6. Finally, cleaning of the joint, in case of any residue left.

In literature, Al-Si filler is most popular among brazing industries, for joining various parts of heat exchanger, automotives and aerospace applications. Therefore, the design of a lower melting brazing filler alloy is a serious concern in

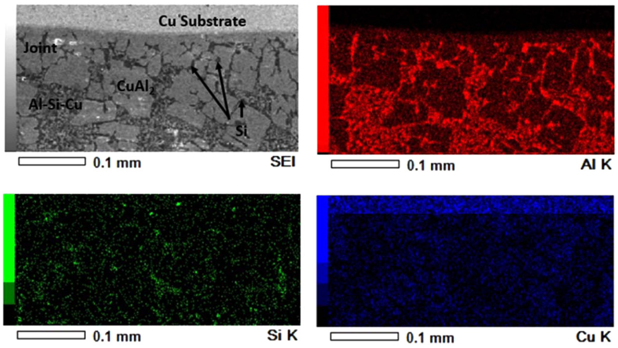

Fig. 2. Al-Cu brazed joint using Al-Si-Cu filler alloy.

brazing industries. The most common composition of Al-Si filler is Al-12 wt %Si in a near eutectic composition with a melting point at 577°C. This melting temperature is in close proximity of the melting point of various aluminium alloys. Therefore, we need a low Al-Si melting filler. Various kinds of Al-Si alloys have been developed by adding elements and other impurities. A number of alloys are available where copper have been added.[26-28)] For example, to lower the melting point copper is primarily used to form Al-Si-Cu alloy.[29)] The microstructure of brazed Al-Cu joint bonded using Al-Si-Cu filler is shown in Fig. 2. The microstructure contains the Si particles and big $CuAl_2$ IMC compounds. The authors have found that $CuAl_2$ are formed at the brazed joint which are not desirable.

The addition of copper is beneficial to depress the melting point, and, at the same time, it produces several undesirable intermetallic compounds like $CuAl_2$. The generation of $CuAl_2$ is not recommended from the brazing point of view as it can generate cracks and fail the joint. In another result the authors have added Zn and Cu in their work to obtain the melting point around 500°C. The microstructure of the brazed joint is given in Fig. 3.

Addition of Zn has also been also tried by a number of researchers in Al-6.5Si-42Zn and Al-6.5Si-42Zn-0.5Sr, with

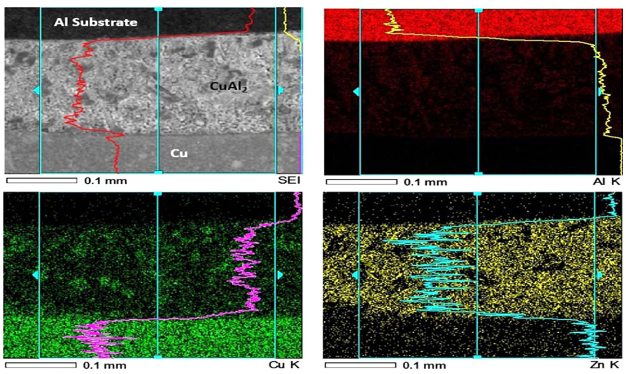

Fig. 3. Al-Cu brazed joint using Al-Cu-Zn filler alloy.

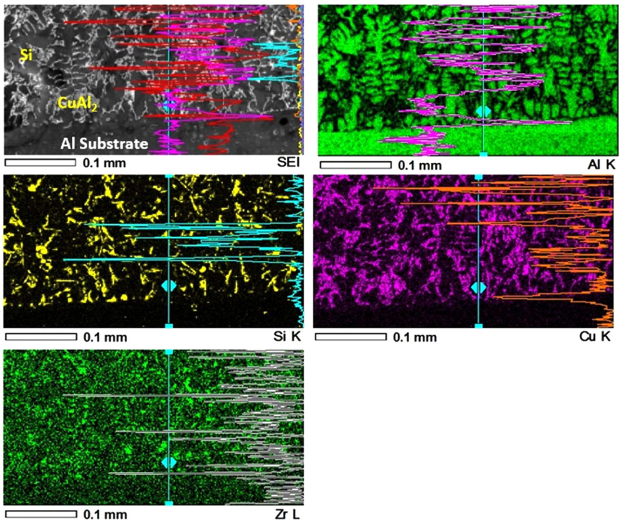

Fig. 4. Al 4047 brazed joint using Al-Si-Cu/ZrO_2 filler alloy.

a significant depression in melting point around 520°C. However, Zn vaporizes quickly generates pores in the joint. In another study, Niu et al. investigated on Al-Si-Ge-Zn alloy and found improved wetting.[34)] The addition of Ge is not a good idea because of extremely higher cost around 400 times than the Al. This makes overall process highly expensive.[35)] Other reports also suggest to combine Cu with Ni, e.g., Al-20Cu-2Ni-5Si with a melting temperature below 538°C and attractive shear strength of the joint greater than 75 MPa.[33)] Recently, nanoparticle reinforced Al-Si alloy have also been developed for low melting brazing, for example, Al_2O_3, ZrO_2, La_2O_3, SiC, etc.[19, 27-32)] Recently, the brazed joint microstructures using ZrO_2 nanoparticle doped fillers are given in Fig. 4. The presence of optimum concentration of nanoparticles (≈0.05 wt%) improves the brazed joint strength by refining the Si needles and dangerous IMC compounds.[29)]

However, the research on multidimensional approaches for soldering and brazing nanofillers is in the beginning stage and more efforts are needed to finally bring nanocomposite fillers in the market in coming future.[26-28, 36)]

5. Conclusions

Alloying elements provide the improved microstructure of aluminium and decides the final properties of the alloy. Microstructural modifications are usually brought about by the precipitates causing an enhancement of the strength and durability at high temperatures. The addition of copper triggers the formation of GP zones from the supersaturated solid solution during aging after heat treatment suitable for aerospace. Silicon provides mostly fluidity and castability and suitable for automotive applications. Magnesium too forms precipitates and increase strengthening of the alloy. Ti and B improves the grain refinement and hence provide additional strengthening. Nickel, though expensive used in minute concentration produces aluminides with copper and aluminium for high-temperature stability. Addition of Mn improves the yield strength and ultimate tensile strength, though a reduction in ductility is also observed. Recently, various reports have shown a beneficial effect of the addition of rare earth elements and nano ceramic oxides to refine the grain size as well as the various IMC and Si morphology. This will also help to fabricate the nanocomposite fillers at mass production scale in coming decades. It can be suggested from this review that an alloying of the aluminium alloys affects the various properties, therefore the selection of alloying element should be exercised depending on its role and suitability for the particular brazing application.

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