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ARTICLE

Morphological Evolution and Development Trend of Brazing Materials

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Abstract: With the high-speed development of manufacturing, the brazing technology is being widely used and turning toward a greenization, high efficiency, automation and high reliability direction. The geometrical morphology of the brazing filler metal plays an important role in guaranteeing the automation and high reliability of the brazing. At present, there are numerous researches on brazing filler metal, many of which are based on the material composition, properties, manufacturability, usage range, etc. However, systematic research about the geometrical morphology of the brazing filler metal is rarely reported. Choosing the perfect geometrical morphology of the brazing filler metal can reasonably optimize the process and improve the brazing quality. In this paper, the geometrical morphology of the brazing material was used as the main line, and the characteristics, application scope, representative systems, preparation methods and current situation of the filiform/strip, stick, bulk, foil tape, powder brazing filler metals, the paste solder, the flux-cored wire, the amorphous and the preformed brazing filler metals were summarized. The powder, flux-cored and amorphous brazing filler metals and suitable filler metal geometries for some common brazing methods were introduced. Research suggests that the developing direction of the morphology of the future brazing filler metal is greenization, high-efficiency, low-cost, adaptation to the requirement of new materials, automation, digitization and intelligence.

Key words: brazing filler metal; flux-cored filler metal; amorphous filler metal; preformed filler metal; composite brazing filler metal

With the rapid development of industrial technology, low-cost and intelligent manufacturing has gradually become the target of advanced equipment. Brazing technology is one kind of near-net forming processing and manufacturing technology, with the advantages of low heating temperature, smooth and beautiful joint, small welding deformation, high production efficiency, wide applicability, and the removable ability after welding. Brazing technology can be used to connect the most complex and precision parts and components, which can significantly reduce the manufacturing cost while improving welding quality [1]. In recent years, brazing technology has been widely applied in many areas such as aerospace, nuclear power, vehicle, machinery, construction, oil and coal, home appliances, medical equipment, instruments and apparatus [2]. For the connection of advanced structural material or complicated structural component, brazing shows its unique technical advantages and can even be the only connection method for some new materials or complex structures[3].

The quality of the brazed joint mainly depends on the brazing material. Brazing material consists of brazing filler metal and brazing flux. Brazing filler metal is the metal or alloy that has lower melting point than base metal and is melted to fill the brazing joint during the brazing process. Brazing flux is the substance that can remove or destroy the oxide film of the brazing area of the parent metal and the brazing filler metal during the brazing process[4].

The quality and performance of brazing material, and the reasonability of application choice play a decisive role in the quality of brazed joint[5]. The morphology of the common brazing materials is shown in Fig.1.

To meet the requirements of joint performance and brazing technology, brazing filler metal should generally have a melting

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Fig.1 Morphology of several kinds of common brazing materials

temperature range lower than the parent metal's melting point, and show good wettability, spreadability, stable and uniform chemical composition, so that the using demand of the brazed joint and the cost requirement of production are fulfilled[6].

In terms of the melting point, brazing filler metal can be divided into soft solder (with melting point lower than 450 °C), brazing filler metal (with melting point higher than 450 °C), and high-temperature brazing filler metal (with melting point higher than 950 °C). In terms of the component, brazing filler metal can be divided into soft solder and brazing filler metal: soft solders consist of Sn-based, Zn-based, Bi-based, In-based, Cd-based, and other filler metals; brazing filler metals consist of Al-based, Ag-based, Cu-based, Ni-based, Mn-based, etc. Brazing filler metals can be manufactured into strap shape, filiform shape, cast stick shape, amorphous or common foil shape, powder shape, annular shape, paste shape, flux-cored wire, and flux-coated rod according to supply requirement[7].

Brazing filler metal is usually used together with brazing flux. The functions of the brazing flux are to remove oxide from the surface of the parent material and the liquid brazing filler metal, protecting the parent material and liquid filler metal from further oxidation, promoting the flowing of filler metal, and improving the wettability of the filler metal on the parent metal's surface. Therefore, brazing flux should possess the ability to remove oxide from the surface of the parent metal and filler metal, and sufficient wettability at brazing temperature. Besides, the melting temperature of the brazing flux should be lower than that of brazing filler metal.

Brazing flux can be divided into two major categories: soft soldering flux and brazing flux. According to the special purpose, brazing flux can be divided into aluminum flux, pulverous brazing flux, liquid brazing flux, gaseous brazing flux, pasty brazing flux, and free cleaning brazing flux.

In the actual brazing process, choosing appropriate brazing material is very important. Choosing the geometry of the brazing material reasonably can greatly simplify the process and improve the quality of brazing. This paper mainly introduces the related features of several brazing filler metals and brazing fluxes with different shapes.

1 Filiform and Strip Shape Brazing Filler Metals

The general form of brazing filler metal is strip or filament. These kinds of brazing filler metals have been widely applied because of their simple joint-method and the simplicity of controlling the brazing seam thickness[8]. Liquid collapse phenomenon will appear while placing filler metal in advance during the brazing procedure. When the filler metal is delivered by hand, it can be added to the brazing seam before the workpiece is heated to the desired brazing temperature so that the fluid collapse can be avoided.

Filiform and strip shape brazing filler metals are suitable for manual brazing, such as iron soldering and flame brazing. Automatic brazing with strong continuity character, such as laser brazing, electron beam brazing, etc, is also conducted using filiform brazing filler metal[9,10]. For closed joint like annular, short brazing seam often uses filiform or strip shape filler metal. For some very fine, complicated tubular joint and extremely precise parts in the jewelry industry, thin filiform filler metal is the best choice[11,12].

The commercial application of filiform and strip silver brazing filler metals has already formed the scale so far. A series of silver brazing wires with different sizes and alloy compositions can be obtained from the market. Tin-based solder wires have been already applied in electronics maturely. The mass production and application of many specifications of tin-based solder wires have been realized early. In addition, a variety of aluminum-based and copper-based filler metals have also been developed successfully for commercial production.

2 Foil Shape Brazing Filler Metal

Foil shape is another common geometry shape of brazing filler metal. This kind of brazing filler metal is suitable for certain occasions such as plain narrow gap because of its flexibility, simple adding method and easy control of the thickness of the brazing seam. Foil shape brazing filler metal is suitable for the regular flat brazed joint, and is hard to use in complicated brazed joint or automatic brazing. Foil shape brazing filler metals are divided into traditional crystal and amorphous foil brazing filler metals. The current research mainly focuses on amorphous foil brazing filler metal.

Foil shape brazing filler metal can be used in the preparation of honeycomb structure. Gao[13] manufactured a round porous structure using BNi82CrSiB crystal foil brazing filler metal to join foil and serrated FeCrAl parent metals in the preparation of automobile burner parts and honeycomb carriers (the assembly method is shown in Fig.2). Under the stereoscopic microscope, both sides of the component were flat, without macroscopic defects on the surface such as obvious oxidation, incomplete penetration, inclusions, pores, and crack, and 99% (the number of joints was about 8000) of the brazing joints were connected. The wettability of brazing filler metal was great. The liquid filler metal filled the gap and

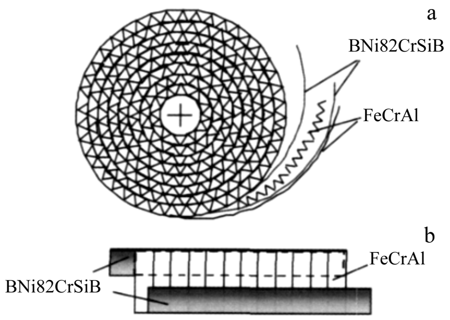

Fig.2 Schematic diagram of assembling brazing sample: (a) top view and (b) position of the brazing filler metal[13]

formed the rounded corner on both sides of the brazing seam.

Foil strip filler metal has certain advantages for brazing large-plane-narrow-gap component. Lin et al[14] have used vacuum brazing assembly to braze gas turbine labyrinth seal rings, with copper-based B-Cu35NiMnCoFeSi(B, P)-S crystal foil as brazing filler metal. The obtained brazing seam surface was uniform, meeting the requirement, and it can be transferred smoothly from the parent metal surface, without defects such as shrinkage cavity, filler metal separation, and non-fusion. Chen [15] brazed Q235 steel and 3003 aluminum alloy using Zn90Al4Ag5Ce crystal foil brazing filler metal to explore the preparation of Al-steel plate-fin heat exchanger. In addition, the brazing process of aluminum alloy slot array antenna and aluminum alloy waveguide can use BAl86SiMg foil as brazing filler metal to attain reliable product quality, high precise dimension, and stabilized usability.

3 Stick and Bulk (Graininess) Shape Brazing Filler Metals

Stick shape filler metal is one kind of the common supply status of brazing filler metal. This kind of brazing filler metal can be attained by casting molten alloy directly, and drawing or extruding the ingot. The production standards of many kinds of alloy system stick brazing filler metals have formed unified criterion systems, which means that they can be produced in accordance with the provisions of the national standard.

Stick filler metal is particularly suitable for iron soldering or flame brazing because of its geometry advantages, which is easy to feed and to realize high brazing efficiency. For example, the Bundy tubes used in automobiles and fridges are brazed by flame brazing. It usually heats the silver brazing filler metal stick and dips in brazing flux first, and then brings the silver stick to the heated parent metal surface. Stick shape brazing filler metal has become a common form of supply for many manufacturers due to its simple production process, mature production technology, and convenient transportation. The surface of finished products should be smooth, without inclusions and oxide skin which can negatively influence the properties of brazing performance. Compared with large length or continuous loading in coil filiform filler metal, stick filler metal is not long enough to suit the automated brazing process, and is easily wasted while using manual brazing.

Bulk or graininess filler metal possesses the advantages of manageable dosage and convenient preset and has a broad application market. The brazing of cutting picks[16] used in coal industry, and dip brazing of polycrystalline diamond compact bit (PDC bit)[17] used in exploration, drilling, and digging need to cut stick or foil filler metals into certain sized bulks, or directly pouring melting alloys into bulk or graininess shape in order to feed the filler metal according the quantity. The brazing of copper bar rotors and end ring of some type of alternating current dynamo[18] belongs to one kind of repetition structure of multi-equal brazing spots. The structure of the altering current dynamo is decades of rotor bars inserted into the holes that arrange in a circle in the end ring. To ensure the consistency of brazing quality, the consistency of dosage of filler metals should be guaranteed, and the same specification bulk brazing filler metal should be chosen to avoid the difference of brazing quality due to different filler metal quantity.

4 Powder Shape Brazing Filler Metal

As brazing techniques are developed to the direction of high efficient and large-scale automatic production lines, the requirements of brazing filler metals become increasingly higher. Traditional filiform and foil shape brazing filler metals are very difficult to meet the technical requirements of the refinement of brazed workpiece, and the diversification and complication of brazing joint, so their applications are limited to a certain degree. Moreover, for some alloy systems that are difficult to melt or cold machine, the manufacture of filiform or brazing filler metal is restricted by technology[19]. Powder or paste shape brazing filler metal possesses the advantages of precise dosage, convenient preset, high- efficiency, and automatic production suitability. It can both satisfy the productive technology requirements of automatic brazing and make high-efficiency automatic brazing into realization. This has become a significant direction of the development of brazing material [20,21].

The manufacture technology control has a significant influence on the quality of powder brazing filler metal, brazing process, and the quality of brazed joint. Essentially, it is important to improve the purity of brazing alloy, the compactness, and homogeneity of the internal structure, and to reduce the inner defects of brazing filler metal as well[22]. At present, the commonly used preparation methods of brazing alloy powder are atomization method, mechanical alloying method, coprecipitation method, etc.

Most of the brazing filler metals can be bought in powder form. When adding powder brazing filler metal to the brazed joint, it is often necessary to use proper adhesive or flux together to make the powder brazing filler metal adhere to the workpiece before brazing. Common powder brazing filler metals are aluminum-based, copper-based, silver-based, nickel-based, etc. The properties can be seen in Table 1[23]. The nickel-based filler metal is very brittle because of the existence of B and Si elements, so it is difficult to be manufactured into various shapes and is often supplied in powder form or powder adhesive tape, such as BNi_2 brazing filler metal. Besides, brazing filler metal that contains refractory metal elements has big processing difficulty and is mainly provided in irregularity powder form[24,25].

In the repair brazing and avoiding inadequate brazing of some complicated components, powder brazing filler metal is used frequently[26]. Using powder brazing filler metal can solve the present difficulty of large area brazing joint. For example, Al-Si eutectic alloy powder was used as filler metal when compounding a layer of aluminum on the stainless steel cooking utensil[27].

5 Paste Shape Brazing Filler Metal

As mentioned above, application of traditional filiform or stick brazing filler metal is somewhat restricted. Paste shape brazing filler metal (also named solder paste) can solve the precise brazing issues of micro-devices, realize automatic operation of brazing, and is easy to add, thus gradually replacing some traditional geometry shape brazing filler metals[28]. The proportion and overall demand of the paste solder in the soldering of the microelectronic device are increasing gradually.

Paste brazing filler metal is a kind of pasty fluid consisting of alloy powder, brazing flux, and binder. In the process of practical production, powder brazing filler metal is often turned into paste to use, which can be regarded as a kind of paste brazing filler metal[29]. Theoretically, any kind of brazing filler metal, such as Cu-P-(Ag), Al-Si, Ag-Cu-Zn, Ni-based, Mn-based, etc, can be manufactured into paste shape. With the development of automatic brazing and the popularization and application of microelectronics packaging technique, the demand of paste brazing filler metal is increasing gradually.

Table 1 Powder filler metals and their performance[23]

Category	Grade	Composition	Melting temperature/°C	
			Solidus	Liquidus
Cu-based	FBCu14	CuSnZnNiMn	740	785
	FBCuSn	Cu82SnNiP	680	900
	FBCu16Ag	CuSnZnAgNiMn	680	760
Ni-based	FBNiCr	Ni88CrSiBP	998	1128
	FBNiCrSiB	Ni74CrSiB	975	1040
	FBNiSiB	Ni92SiB	980	1040
	FBNiCrCu	NiCrCu	980	1020
Al-based	FBAl88Si	Al88Si	577	580
	FBAl90Si	Al90Si	580	592
Ag-based	FBAg	Ag99CuPB	958	960
	FBAg737	AgCuZnCdNiCo	610	688
	FBAg625	AgCuZnSnNiCo	670	750
	FBAg518	AgCuSnNiP	580	680
	FBAgCuSn	AgCuSn	620	725

Paste brazing filler metal usually consists of alloy powder and brazing filler metal carrier. The carrier includes soldering flux, solvent, activator, the medium that regulates rheological properties, etc. Brazing alloy powder is the main source of the brazing seam metal, the shape of the powder is mainly spherical, and the size of the powder should be as homogeneous as possible[30,31]. According to the melting temperature, brazing paste can be divided into high-temperature brazing paste (melting point is higher than 250 °C), normal solder paste (melting point is 179~183 °C), and low-temperature solder paste (melting point is lower than 150 °C). According to the composition of the alloy powder, brazing paste can be divided into many categories, such as, tin-lead system, tin-lead-silver system, tin-silver system, etc.

The usage of brazing paste is convenient, but the production and storage requirements are high. Paste brazing filler metal should possess the chemical properties of nonmiscibility and immiscibility in a certain period of time and at general surrounding temperature in order to avoid the defects such as heterogeneous composition, poor oxidation resistance and difficult storage caused by the separation of alloy powder, brazing flux and binder. Although various brazing pastes have been produced in abundance by many domestic corporations, the current domestic production of brazing paste cannot fully meet the needs of users, and manufacturers also need to import brazing paste from abroad. Since the cost of imported brazing paste is high, the procurement cycle is long and the quality of brazing paste is difficult to guarantee, the normal proceeding of production is seriously affected. Therefore, it is significant to strengthen the research and development of brazing paste, so as to adapt to the demand of the market.

6 Flux-cored Wire Brazing Filler Metal

The normally used filiform brazing filler metal is solid wire metal or alloy material, which needs the addition of brazing flux in the procedure of using. The brazing flux should be coated in advance manually on the brazed joint and the solid wire brazing filler metal also should be pre-set before the brazing workpiece is heated. Coating brazing flux may manually increase the brazing cycle period and generate a variate because of adding a pre-brazing operation, thus affecting the consistency of connection and stability of the quality. Coating brazing flux manually also increases the cleaning time and produces potential safety hazard. In order to solve these problems, flux-cored brazing filler metal is introduced into the brazing industry. Flux-cored brazing filler metal can guarantee the consistency of the process and improve the quality of brazed joint while reducing brazing time period and potential unsafety or environment hazard[32,33]. As a high-tech achievement in brazing field, the appearance and development of flux- cored brazing filler metal have adapted to the trend of high efficiency, low cost, high quality, automatic and intelligent brazing[34,35]. The morphology of flux-cored brazing filler metal is shown in Fig.3.

Compared with the traditional brazing materials, flux-cored brazing filler metal has the following advantages: self-fluxing, high brazing efficiency, flexible composition, energy and material saving, less brazing flux consumption, low cost, less pollution, excellent brazed joint, and direct continuous brazing[36,37].

Limited by the industrial scale and processing level of brazing material, the development of flux-cored brazing filler metal is relatively slow and still in its infancy. Currently, the research about flux-cored brazing filler metal is mainly focused on Al-based material, and the report that can be retrieved about other alloy system brazing filler metal is really less[38]. The successful research and development of flux-cored Al brazing wire have partly solved the problems of generating Cu/Al brittle phase joint, considerably different thermal expansion coefficient and electrode potential while brazing Al-Al and Al-Cu. So flux-cored Al brazing wire is widely used in aerospace, automobile, electronics, living goods, etc[39].

In recent years[39], the American, German and Korean substantial welding material companies have consecutively launched the flux-cored Al brazing wire used for Al-Al brazing and Al-Cu brazing, mainly Al-Si system and Zn-Al system. They play a significant role in brazing Al-Al or Al-Cu alloys. The research and development of flux-cored Al brazing wire in China are almost synchronous with the advanced international institutions. Zhengzhou Research Institute of Mechanical Engineering Co., Ltd has always been a pioneer in the research and development of flux-cored brazing material of China who exhibited flux-cored steel welding wire in 1958. In terms of flux-cored Al brazing wire, it has also laid the foundation for the application of flux-cored brazing material in China. Zhengzhou Research Institute of Mechanical Engineering Co., Ltd has been equipped with the basic conditions for industrial production of flux-cored Al brazing wire. The economic feasibility of replacing some Al-based brazing materials with flux-cored Al brazing wires has passed the production verification[40].

Fig.3 Morphology of flux-cored brazing filler metal

At present, the silver brazing wire is largely used in refrigeration, electricity, and electrical equipment. With the development of automatic brazing replacing high-cost manual brazing, the dosage of silver brazing filler metal is controlled more and more precisely. Therefore, seamed and seamless flux-cored Ag brazing wires have emerged under this industrial updating demand. On account of the cost control of automatic brazing manufacture, the requirement of developing trend of substituting Cu for Ag, and the consideration of environment problems, Cu-based flux-cored brazing filler metal has also risen in response to the proper time and conditions.

In view of its great advantages, flux-cored brazing filler metal has broad application in air conditioning refrigeration, electricity, electric appliance, etc. At present, the research and development of multi-alloy system flux-cored brazing materials are the urgent problem to be solved. The research system of flux-cored brazing filler metal is relatively thin. Though there are patented reports about flux-cored silver brazing material, which have possessed a huge market space, the mass production and application of it have not been seen. The most urgent thing is to accelerate the research progress of flux-cored brazing filler metal to make up for the application deficiency in sliver brazing material field. In addition, the matching problem between brazing filler metal and brazing flux should be solved in order to manufacture flux-cored brazing materials with comprehensive alloy system and mature technology.

7 Amorphous Foil Shape Brazing Filler Metal

For some alloy systems that are difficult to melt and cold process, the manufacture of brazing filler metal is limited. Some brazing filler metals used in traditional brazing contain expensive silver and toxic cadmium that can increase the cost and pollute the environment. Some of the brazing filler metals can be only supplied in powder form because of its brittleness. The used brazing flux and binder tend to make brazing seam generate defects like pores and inclusions[41]. Amorphous foil brazing filler metal has been widely used because of its advantages, such as uniform composition, good wettability and mobility, no binder and other impurities, high alloying degree, easy clipping, low melting temperature range, conductive to industrial application, etc[42].

Amorphous brazing filler metal is a new kind of brazing material developed in the 1970s[43,44]. This kind of brazing filler metal makes brittle alloys such as nickel-based alloy, copper-phosphorus, and copper-titanium that cannot be stretched able to be manufactured in foil shape. Amorphous foil brazing material can meet the requirements of flat brazed joint and have significant effect on brazing technology development. Amorphous brazing material possesses good adaptability, and has been successfully applied to the vacuum brazing or resistance brazing of cooler, radiator, honeycomb structure, silencing device, electronic device, and ceramic-graphite joining[45].

Since the invention of amorphous brazing material, it has gained the favor of brazing industry because of its excellent performance. Under the unremitting efforts of scientific research and development staffs, hundreds of nine-big-series amorphous brazing materials including Ni-based, Cu-based, Cu-P-based, Pd-based, Sn-based, Pb-based, Al-based, Ti-based, Co-based have been developed and widely used in salt-bath dip brazing, vacuum brazing, furnace brazing, and transient liquid phase diffusion welding abroad. In China, the amorphous brazing materials that have access to the national standard are 7K301 (Ni-based), 7K701 (Cu-Si-Ni system), 7K702 (Cu-Ni-Sn-P system) and 7K703 (Cu-Ag-Sn-P system). Other alloy system amorphous brazing materials are also reported.

Ni-based amorphous brazing material is one of the most promising brazing material. It can be applied to the brazing of various high temperature alloy, high-alloy steel, and stainless steel with ceramic in many fields like aerospace, atomic energy, and mechanical industries[46,47]. At present, it has been widely used for brazing in nuclear power plant fuel compartment, gas turbine regenerator, static guide vane of turbine generator, plate-fin engine oil cooler, radiator, precision device, etc.

Cu-based amorphous brazing material can replace silver based brazing filler metal applied in the brazing of Cu-Cu alloy, Ag-Ag alloy, and various contact materials because of its uniform composition, low melting temperature, good mobility, and enough flexibility to required shape. Cu-based brazing filler metal without phosphorus element can be used in brazing low-carbon steel, and currently maximum applications include the brazing of various low-voltage electrical contact material, conductor, commutator, protector, temperature controller, and transformer of the continuous current dynamo[48].

The low-temperature amorphous brazing filler metals mainly contain Al-based and Sn-based materials, and are applied in the brazing of electric industry, printed circuit, semiconductor device, etc. Ti-based amorphous brazing filler metal is very efficient in brazing diamond, graphite and ceramic materials[49]. The general situation of common amorphous brazing filler metals is listed in Table 2[48-54].

Rapid solidification is the main method for preparing amorphous brazing material. Rapid solidification possesses the advantages of high alloying degree, low impurity content, little elemental segregation, and easiness of application. This method has pointed out the direction for the manufacture of the brittle brazing materials, attracting people's high attention in recent years with very optimistic prospect of development[55].

For the last decade, the United States and Japan have accelerated the development of amorphous alloys, and China has also increased the research and application in this field. Amorphous brazing material has excellent and unique performance and extensive application prospect. The application of it can solve the technical and material bottleneck problems of China in many fields. It has greatly promoted the development of brazing technology and materials. Without doubt, it has played a positive role in the progress of China's industry and national defense.

Table 2 Commonly used amorphous filler metals and their application[48-54]

Amorphous brazing filler metal	Representative alloy system	Appropriate parent materials	Current and future use
Ni-based	Ni-Si-B Ni-Cr-B-Si	Stainless steel, steel-nickel alloy, low alloying steel	Aero-engine components, heat exchanger, diamond instrument, dental braces
Cu-based	Cu-Ag Cu-Sn Cu-Ni-Ti Cu-Ni-Sn-P	Copper-copper alloy, low carbon steel, stainless steel, ceramic	Heat exchanger, auto parts, electric contactor, transmission, etc
Al-based	Al-Si Al-Cu-Si Al-Ge-Si	Aluminum-aluminum alloy, steel-aluminum alloy	Aeronautic honeycomb structure, auto radiator, heat exchanger, etc
Ti-based	Ti-Zr-Cu Ti-Cu-Ni Ti-Zr-Cu-Ni	Titanium alloy-steel, ceramic	Aeronautic structural component, missile fin, engine, honeycomb structure, titanium tube
Fe-based	Fe-Si Fe-Si-B Fe-P-B Fe-Al-P	Ferrous-ferrous alloy, steel, ceramic	High-frequency magnetic core, transformer, inductor, mutual inductor

8 Special Geometry Shape Brazing Filler Metal

In addition to some common geometry shape brazing filler metals mentioned above, another brazing filler metal can also be manufactured into special geometry shape according to the specific use or preparation situation, which is the so-called preformed brazing filler metal. Preformed brazing filler metal is customized according to the special shape of brazed joint. The commonest shape is annulus, and besides that there are square, trapezoid, sector, arc, H shape, U shape, bar type, rotundity, etc[23] (Fig.4). It is also feasible to mix nickel based powder brazing filler metal or other alloy system powder with binder according to a certain proportion to make the new super thin preformed brazing filler materials stick with solder. Stick with solder is a great progress in the manufacture technology of brazing materials, apart from the advantages of paste brazing material. It also possesses the characters of easiness to use, operate, and control[56]. Furthermore, a high Zn content AgCuZn alloy with poor forming property was in-situ synthesized using AgCu/ ZnCu/AgCu sandwich sheet during the induction brazing process. AgCuZnSn sandwich brazing material was in-situ synthesized using AgCuZn (high silver low zinc) sheet and ZnCuAgSn (high zinc and tin and low silver) sheet through the same way, solving the difficulty of manufacture caused by the plastic property decrease of AgCuZn alloy after adding Sn element[57].

In the brazing process, the preformed brazing material is easy to realize automatic assembly and employ, and is quite efficient. The geometry size of the brazing filler metal is in accordance with the brazing seam, so the loss of the brazing material is little during the wetting spread progress. The utilization factor of the brazing material is high, thus reducing the usage amount of brazing material. With the requirement of brazing material geometry size, surface roughness is getting increasingly higher, and the workpiece brazing seam shape is also more and more varied. The geometry shape and size of the preformed brazing material are unable to unify, which increases the manufacturing cost of the brazing material.

9 Brazing Flux and Its Geometrical Morphology

Generally speaking, it is important to completely remove the oxide films on the parent material and brazing filler metal surface in order to realize the brazing process and obtain ideal brazing quality[58].

Fig.4 Morphology of the preformed filler metal

Brazing flux can remove the oxide films on the surface of the substrate metal and liquid brazing filler metal, protect them from oxidizing again while heating, improve the wetting property between brazing filler metal and parent metal, and promote the flowing of brazing filler metal. Moreover, brazing shielding gas provides an active or inert protection atmosphere around the workpiece, which can be seen as one kind of special brazing flux[59,60].

The composition of brazing flux mainly depends on the physical and chemical properties of the oxide to be removed. The matter constituting brazing flux can be a single component (such as borax, zinc chloride) or a multi-group system. The multi-group system normally consists of matrix component, membrane removing component, and active component[61].

From different perspectives, brazing flux can be divided into various types[62]. For example, according to the using temperature, it is divided into soft brazing flux and hard brazing flux; according to usage, it is divided into ordinary brazing flux and special brazing flux; according to the supply form, it is divided into powder brazing flux, liquid brazing flux, gas brazing flux, paste brazing flux, and no-clean brazing flux, etc.

Powder brazing flux. Powder brazing flux is one of the most commonly used supply forms of the flux. It possesses the advantages of simple production process, convenient adding and controlling, and easiness to store and transport[63]. Powder brazing flux is often mixed with water or alcohol to form paste state and it can also be sprinkled in a dry form on the brazed joint surface. Alternatively, it is possible to insert the heating brazing filler bar into the container of the dry powder brazing flux to pick up some powder brazing flux for using. The dry powder brazing can also be used as the chemical groove of the dip brazing. However, some traditional brazing fluxes (such as homemade QJ102, QJ103) contain mass of KBF4, which is easy to dissolve in water and undergoes drastic hydrolytic reaction. Therefore, this kind of brazing flux (QJ102 or QJ103) is inclined to absorb moisture, and since KBF4 hydrolytic reaction occurs after moisture absorption (or adding water to make paste), the effect of the brazing flux disappears.

Paste brazing flux. Paste brazing flux is also one of the most commonly used supply forms. It is generally made by mixing wetting agent into powder brazing flux, and can be adhered to the brazed joint or workpiece before brazing, so it has better maneuverability compared to powder brazing flux. Paste brazing flux is not suitable for storage. It will separate after long time placement, and it needs to be mixed with the brazing flux compound before use. Paste brazing flux can be diluted with water, but its preparation should avoid any compounds that may react with water, because the reaction will result in the performance deterioration or failure of the brazing flux.

Liquid brazing flux. Some brazing fluxes can be completely dissolved in water and can be made into liquid solutions called liquid brazing flux. Liquid brazing flux is almost exclusively dedicated to flame brazing. Fuel gas will carry brazing flux while passing through the container of liquid brazing flux. Using this flame to heat the workpiece, the brazing flux can be applied to the desired area. Liquid brazing flux is difficult to store and transport. It is often prepared and used simultaneously.

Brazing flux for solder can be divided into three categories: resin, organic and inorganic, in the forms of liquid, solid or paste. Inorganic soldering flux is generally liquid or paste state, such as zinc chloride solution (FS312A), zinc chloride-ammonium chloride solution (FS311A), paste soldering flux and phosphoric acid, etc. Organic soldering flux is mainly liquid or paste state, such as water solubility organic soldering flux which is liquid. Resin soldering flux is mainly paste generated by dissolving powder soldering flux in alcohol, or organic solvent. Hard brazing flux can be divided into four categories: powder, paste, liquid and gas, according to its geometry form. For the manufacture of powder and paste brazing flux, the grinding method is currently mostly adopted in China. Mixing wetting agent with powder can prepare paste brazing flux.

The oxide film of the aluminum surface is compact and stable. Specialized brazing flux must be used for brazing aluminum and aluminum alloy, which is the brazing flux for aluminum[64]. Brazing flux for aluminum includes soft brazing flux and hard brazing flux. Soldering flux for aluminum can be divided into organic soldering flux and reaction soldering flux. Organic soldering flux generally consists of amine organics, such as trienthanolamine solvent added with several kinds of borofluoride. It is usually in paste form without hygroscopicity, and will dry out gradually if exposed to air atmosphere. Reaction soldering flux for aluminum mainly consists of the chloride of heavy metals such as zinc and tin. A little amount of halide of potassium, sodium and lithium may be added to improve the activity[65,66]. It usually contains ammonium chloride and ammonium bromide to decrease its melting point and to improve its wettability, generally in powder state, like QJ203. Brazing flux for aluminum is usually in powder forms, such as frequently-used QJ201, QJ202, QJ206, QJ207, and other fluoride brazing flux.

Gas brazing flux is a special type of flux. It can be divided into brazing flux for furnace brazing and flame brazing according to the brazing method. The greatest advantage of this kind of brazing flux is that there is no flux residue after brazing, so the brazed joint does not need to be cleaned. However, this kind of brazing flux and its reactants mostly have a certain toxicity, which requires corresponding safety measurements.

10 Domestic and International Production Situation of Brazing Materials

Brazing material has always been one of the focuses of brazing research. The research and development of brazing material have a long history. Foreign countries have started the research and production of brazing material very early, so the technology has been relatively mature. They have formed a certain industrial scale.

After nearly three decades of rapid development of Chinese industry, the production, research, and development of brazing material have made great progress, but there is still a big gap compared with developed industrial countries like the United States, Germany, and Japan. Domestic brazing material industry is still in its adolescence. There are a number of enterprises, but the qualifications are uneven, and the scale difference is significant. Most small brazing material manufacturers still stay in the lower-level competition of small-scale and imitation production. Only a small number of enterprises are in a leading position in the market competition through independent research, development and technical improvement.

11 Conclusion and Expectation

In summary, brazing filler metals are often processed into different geometry shapes according to the requirements of brazing process and material processing properties, and choosing proper geometry shape of brazing filler metal can simplify the process and improve the brazing quality. The geometry shape of brazing filler metal is usually determined on the basis of brazing method, brazed joint character, and production quantity. For example, iron soldering and flame brazing used brazing filler metals are usually fed-in by hand, so the stick, strip, filiform, and tube shape brazing filler metals are applicable. Resistance brazing usually chooses foil shape brazing filler metal. Induction brazing and furnace brazing often use filiform, annulus, gasket, powder and paste shape brazing filler metals. It is advisable to use clad brazing sheet in salt-bath brazing. Moreover, a closed brazed joint like annulus usually uses filiform brazing filler metal. For smallish brazing seam, filiform and graininess shape brazing filler metal can be used. And for large area brazed joint, powder or foil shape brazing filler metal should be chosen.

In addition, in the process of brazing filler metal production, the supply conditions of different alloy system brazing filler metals are different because of the processing performance difference of different metals or alloy systems. For example, tin-based brazing filler metal can be manufactured into filiform, stick, foil shape, and active rosin cored wire. Aluminum-based brazing filler metal is usually supplied as filiform, stick, foil and powder shape. It can also be made into bimetal (Al-Si) composite board and used for large area brazed joint and joint-intensive parts like heat exchanger to simplify the brazing process. Silver-based filler metal is often supplied as stick, filiform, strip, and foil shape. Nickel-based and cobalt-based brazing filler metals contain a large amount of Si, B, P non-metallic elements, which will form many boride, silicide and phosphide brittle phases. Therefore, the process deformability of these alloys is poor. They are difficult to be made into filiform or foil shape and often supplied as powder shape. In recent years, They have been developed as an amorphous foil brazing filler metal and an adhesive tape brazing filler metal. Copper phosphorous brazing filler metal (BCuP) can be supplied as filiform, graininess, preformed, and paste shape. Titanium-based brazing filler metal has poor processing performance because of its brittleness, which is difficult to be made into foil shape and mainly supplied as powder or paste shape initially, and then developed into thin sheet stacking and amorphous foil shape. Iron-based brazing filler metal is cheap and usually supplied in powder shape. The complexity of the brazing workpiece structure sometimes requires manufacturing the brazing filler metal into a more suitable geometry shape; therefore, it is necessary to fully consider whether the processing performance of the material can meet the requirements of desired form when choosing.

Based on the development of material processing technology, brazing automation technology, and compliance with the environmental protection requirements, brazing materials are developing in a diversified direction of greenization, cleanness, standardization, diversification, economization, etc. Therefore, the production of low-cost manufacturing and green brazing material will be a mainstream trend in future research. The composite brazing materials like flux-cored brazing material and amorphous brazing material are the main focus of the present study and may have a large market space. It is needed to promote advanced manufacturing technology actively and to improve the production equipment and product quality. The companies should accelerate the construction of research and development capabilities, use technology to dominate products, pay attention to independent innovation and integrated innovation simultaneously, accelerate the pace of industrialization of achievement, and develop products that are efficient, green, environmentally friendly, and adaptable to the new development trend of new engineering materials and brazing automation brazing materials.

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钎焊材料形态演变及发展趋势

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摘　要：随着制造业高速发展，钎焊技术应用越来越广，并向绿色化、高效化、自动化和高可靠方向发展。钎焊材料形态对钎焊自动化和可靠性起着至关重要的作用。目前有关钎料的研究主要基于成分、性能、工艺性及应用领域等方面。对于钎料形态方面的系统研究还鲜有报道。在钎焊过程中，采用恰当形状的钎料，可以优化工艺和提高钎焊可靠性。以钎料几何形态为主线，系统总结了丝状/条状、棒状、粒状、箔带状、粉末状、膏状、药芯型、非晶态及预制成形等钎料的特点、应用范围、主要代表体系、制备方法及发展现状，重点阐述了粉末、药芯型和非晶态等钎料以及常用钎焊方法所适用的钎料形态。研究认为：未来钎焊材料形态发展方向是绿色、高效、低成本并适应新材料、自动化、数字化及智能化需求。

关键词：钎焊材料形态；药芯钎料；非晶态钎料；预成形钎料；复合钎料

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