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ARTICLE

Effects of Ga and Ce on the Microstructure and Properties of Cadmium-free Silver Filler Metals

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Abstract: Effects of Ga and Ce additions on the microstructures and mechanical properties of Ag17CuZnSn-*x*Ga-*y*Ce filler metals and brazed joint were investigated by SEM, EDS and tensile test. The results indicate that the solidus and liquidus temperatures of filler metals decrease with addition of Ga and Ce. And the wettability of filler metals on the brass and stainless steel improves when the content of Ga and Ce are 2 wt% and 0.15 wt%. The highest shear strength of brazed joint is 3% higher than the shear strength of the Ag17CuZnSn-2Ga. During brazing process, Ga has a higher diffusion coefficient into stainless steel than other elements. A novel $Ce_{20}(Ag, Cu)_{40}Sn_{40}$ intermetallic phase is found in filler metal when the content of Ce is higher than 0.3 wt%.

Key words: low-silver brazing filler metal; microstructure; rare earth element; shear strength

Silver-based filler metals are the most commonly used materials for general purposes since they can easily braze ferrous and non-ferrous metals, and also provide a sound joint which possesses perfect processing property as well as sufficient mechanical strength[1,2]. Among the silver-based filler alloys family, AgCuZnCd series alloys were widely used in manufacturing industry[3,4], because the addition of cadmium to Ag-Cu-Zn filler metals will obviously reduce the solidus temperature and melting range, and improve the fluidity of the brazing filler alloys[5]. However, according to the European Union directives on WEEE and RoHS, Cd has been forbidden to be used in the silver-based brazing filler metals, which results in the development of new Cd-free brazing filler metals worldwide[6]. So far, several silver-based filler metals, such as AgCuZnSn, AgCuIn, and AgCuInSn have been developed as the alternatives. With the increase of In content, the solidus and liquidus temperatures of silver brazing filler metals decreased obviously. And the wettability of filler metals on copper is improved with addition of In. Nevertheless, the high price of In restricts further application of Ag-Cu-In filler alloy.

The hybrid structure of brass and stainless steel can offer additional advantages over conventional materials, because they possess the high mechanical properties of stainless steel and the excellent ductility of brass. The melting point of Ga is 29.76 °C and the addition of Ga into copper leads to reduction of the melting temperature of alloys[7]. Rare earth (RE) elements are called the "vitamin" of metals, which means that a trace amount of RE elements can significantly enhance the properties of metals[8]. In this study, Ga and Ce were added into the Ag17CuZnSn filler metals to form novel brazing alloys. After that, the effects of trace amount of Ga and Ce on the microstructure and properties of Ag17CuZnSn filler metals in brazing H62 brass and 304 stainless steel were studied. The relationship between microstructure and mechanical properties were elucidated.

1 Experiment

Six kinds of Ag17CuZnSn-*x*Ga-*y*Ce filler metals were prepared from oxygen-free copper, silver, zinc, tin and gallium (99.9 wt% purity). And Cu-20Ce master alloy was

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used as raw materials. Melting process was performed in graphite crucibles by using a medium induction furnace, with the charcoal as the cover material to prevent the melting alloys from oxidizing. The designed composition of the silver-based filler metals used in this study is listed in Table 1. The solidus and liquidus temperatures of silver-based filler metals were tested by DSC.

H62 brass and 304 stainless steel were used for the spreading and brazing test. The substrates were cut into sheets with dimensions of 40 mm × 40 mm × 2 mm and 80 mm × 25 mm × 3 mm. In the spreading test, the silver filler metal (0.2 g) was put on the top surface of the substrate sheet and FB102 flux was applied. The spreading test was conducted based on the China's National Standard GB/T 11364-2008[9]. The spreading test was carried out in the VULCAN 3-130 electrical resistance furnace at temperature of 830 °C for 1 min. The spreading area was calculated using the software Image-Pro Plus.

Flame brazing method was used in study for brazing H62 brass and 304 stainless steel. The shear strength of brazed joints was tested using SANS-CMT5105 electromechanical universal testing system. The constant loading rate of 5 mm/min at room temperature was applied in shear strength test. The shear strength testing were conducted based on the China’s National standard GB/T 27552-2011[10].

After brazing, the cross-section of brazed joint was mounted and etched with the composition of $(NH_4)_2S_2O_8$(15 g) + H_2O (100 mL) + $NH_3{\cdot}H_2O$ (2 mL). The etching time was between 20 s and 25 s. The mounted filler metals and brazing joints samples were checked using a ZEISS ΣIGMA 500 scanning electron microscope and INCA X-Act energy dispersive spectrometer.

2 Results and Discussion

2.1 Melting temperature and wettability of the novel silver filler metals

The solidus and liquidus temperatures of Ag17CuZnSn-*x*(Ga, Ce) brazing filler metals obtained from DSC are shown in Fig.1. The solidus and liquidus temperatures of filler metals were suppressed by increasing Ga and Ce content. When the contents of Ga and Ce are 6 wt% and 0.5 wt%, the solidus and liquidus temperatures of brazing filler metal decreased to 686.1 and 791.2 °C, respectively. The decrease of both solidus and liquids temperatures is believed to be attributed to the low melting temperature of Ga.

Usually, the wettability is judged by the spreading area of a brazing filler metal on the substrate, which indicates that the lager the spreading area, the better the wettability[11]. Fig.2 shows the spreading areas of brazing filler metals at the temperature of 830 °C in air with FB102 flux. It is indicated that the spreading area significantly increases with addition of Ga and Ce. The wettability of filler metal on H62 brass and 304 stainless steel parent materials tends to be improved, namely, the spreading area increasing. As an active element[12], rare earth element Ce tends to accumulate at the solder interface in the molten state, and thus the surface tension of molten brazing filler metal is decreased effectively, which plays an important role in the improvement of the wettability. However, the content of Ce higher than 0.5 wt% into the brazing filler metal, deteriorates the wettability of filler metals. Because Ce is easily oxidized during melting, an increase in the amount of Ce means an increase in the amount of oxides and inhibits the wetting behavior.

Table 1 Chemical composition of silver filler metals (wt/%)

Filler metals No.	Ag	Cu	Zn	Sn	Ga	Ce
1	17	Bal.	35.21	2	1.0	0.1
2	17	Bal.	34.15	2	2.0	0.1
3	17	Bal.	34.14	2	2.0	0.15
4	17	Bal.	34.12	2	2.0	0.3
5	17	Bal.	34.05	2	2.0	0.5
6	17	Bal.	33.96	2	6.0	0.5

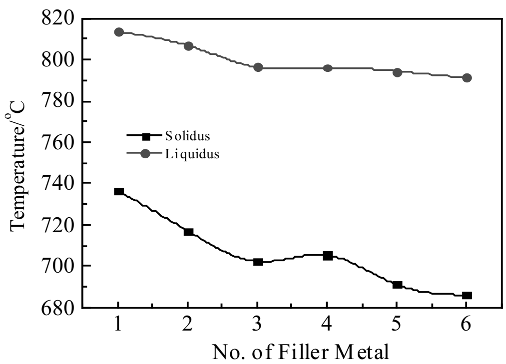

Fig.1 Thermal behavior of low silver filler metals

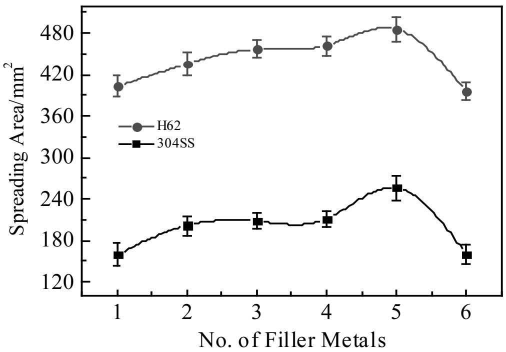

Fig.2 Spreading areas of low silver filler metals

2.2 Microstructure of silver-based filler metals

Fig.3 shows the SEM micrographs of low silver filler metals with different contents of Ga and Ce. As previous studies[13] indicated the low silver brazing filler metals are mainly of composed CuZn compound phase and Ag-Cu eutectoid phase composed (Ag based solid solution and Cu based solid solution). It is clearly found from Fig.3 an obvious microstructure variation of the brazing filler metals with the addition of Ga and Ce. The size of CuZn compound phase in Ag17CuZnSn-1Ga-0.1Ce is larger than that of other alloys. The large brittle CuZn compound phase deteriorate the mechanical properties of brazing filler metal. By comparing the microstructure of Fig.3a~3e, it is indicated that the bulky size of CuZn compound phase turned into fine and dispersive gradually with the addition of Ce. However, lots of bright phases were found in the filler metals around the grain boundary when the content of Ce was in the range of 0.15 wt% and 0.5 wt% as shown in Fig.3c~3f. The SEM high magnification micrograph of microstructures of low Ag filler metals are shown in Fig.4. And in order to clarify the phase constitution of Ag17CuZnSn-2Ga-0.15Ce and Ag17CuZnSn-6Ga-0.5Ce, EDS analysis was carried out under certain conditions. And the EDS results of Fig.4 are shown in Table 2. The contents of Ga in point E and F are seriously higher than others points. It is indicated that point E with around 30.81 at% Ag, 21.29 at% Ce and 37.52 at% Sn is Ce-riched phase. According to the system of Ce-Ag-Sn, this new phase should be the $Ce_{20}(Ag, Cu)_{40}Sn_{40}$ phase[14]. Fig.5 shows the isothermal section at 750 °C of the Ce-Ag-Sn system. The high magnification SEM microstructures and the elements mappings of Ag17CuZnSn-6Ga-0.5Ce filler alloy using the EDS are shown in Fig.6. It can be found obviously that the Ce and Sn cumulate in the bulk phase and the Ag-riched phase surround the rare-earth phase.

2.3 Microstructure of brazed joint bearing different contents of Ga and Ce

There were no micro-cracks in the brazed joint, when Ag17CuZnSn filler metals were used for brazing H62 brass and 304 stainless steel. Fig.7 shows the microstructure around the interface between brazing seam and stainless steel and the elements line scanning. According to Fig.7a,

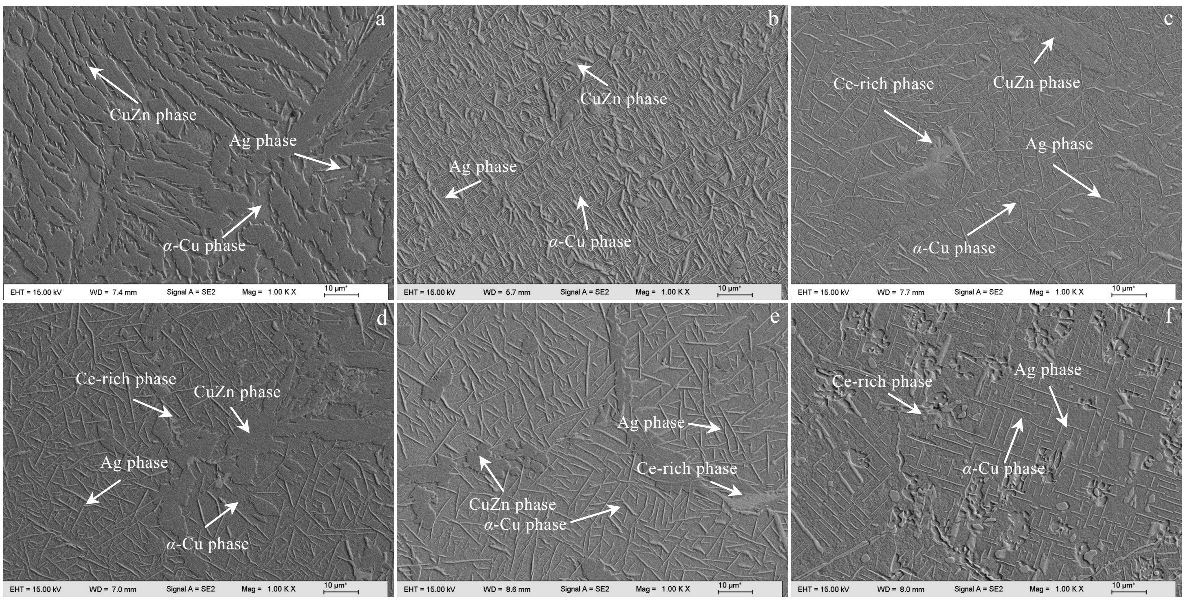

Fig.3 SEM images of low Ag filler metals as cast: (a) Ag17CuZnSn-1Ga-0.1Ce, (b) Ag17CuZnSn-2Ga-0.1Ga, (c) Ag17CuZnSn-2Ga-0.15Ce, (d) Ag17CuZnSn-2Ga-0.3Ce, (e) Ag17CuZnSn-2Ga-0.5Ce, and (f) Ag17CuZnSn-6Ga-0.5Ce

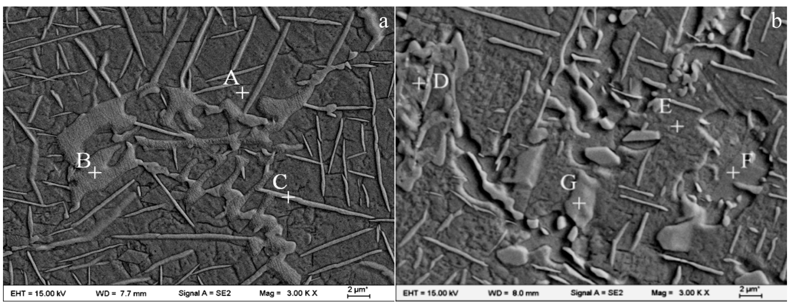

Fig.4 High magnification SEM micrographs of low Ag filler metals: (a) Ag17CuZnSn-2Ga-0.15Ce and (b) Ag17Cu ZnSn-6Ga-0.5Ce

Table 2 EDS results for the points indicated in Fig.4 (at%)

Points	Ag	Cu	Zn	Ce	Sn	Ga
A	7.26	54.00	36.63	0.14	0.76	1.21
B	25.67	14.15	6.56	21.36	32.14	0.12
C	46.11	21.07	30.37	0.18	1.42	0.85
D	20.52	19.81	6.96	23.09	28.21	1.41
E	7.19	54.88	32.71	0.15	0.31	4.76
F	8.86	51.57	29.62	-	1.86	8.09
G	48.82	14.46	32.48	0.23	2.44	1.57

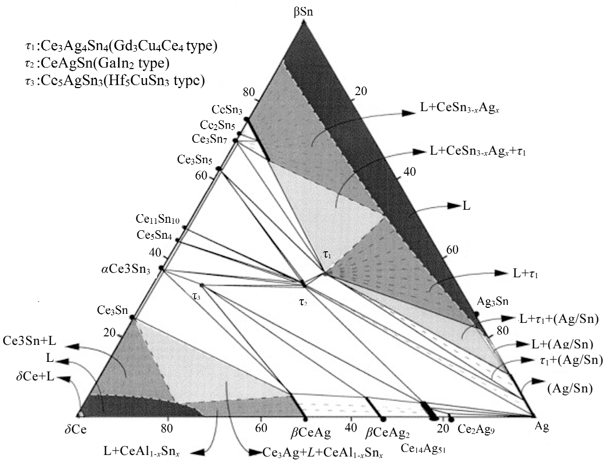

Fig.5 Isothermal section at 750 °C of the Ce-Ag-Sn system

the microstructure of brazed joint consists of two different phases: dark phase (Ag-based solid solution and Cu-based solid solution), and light gray phase (Cu-based solid solution and CuZn compound phase). The EDS line scanning results demonstrate that there are obvious element diffusion between brazing seam and stainless steel during brazing process. Moreover, Ga has a higher diffusion coefficient into the stainless steel than Ag, Cu, Zn and Ce.

The width of interfacial element diffusion during brazing process is around 1 μm. However, the grain boundary permeation is found around the interface when using Ag17CuZnSn-*x*Ga-*y*Ce filler metal for brazing. And the severe grain boundary permeation will deteriorate the mechanical properties of brazed joint[15].

2.4 Effects of Ce and Ga modification on the shear strength of brazed joints

The shear strength of brazed joint and average values are plotted in Fig.8. To ensure the accuracy of the results, three specimens were brazed with the same silver filler metal and under the same brazing conditions. The error bar comes from three trials. The highest shear strength of brazed joint is 378.6 MPa using Ag17CuZnSn-2Ga-0.15Ce for brazing. For comparison[16], Ag17CuZnSn-2Ga was also used for brazing under the same condition, and the brazed joint achieved a shear strength of 367.5 MPa. However, the shear

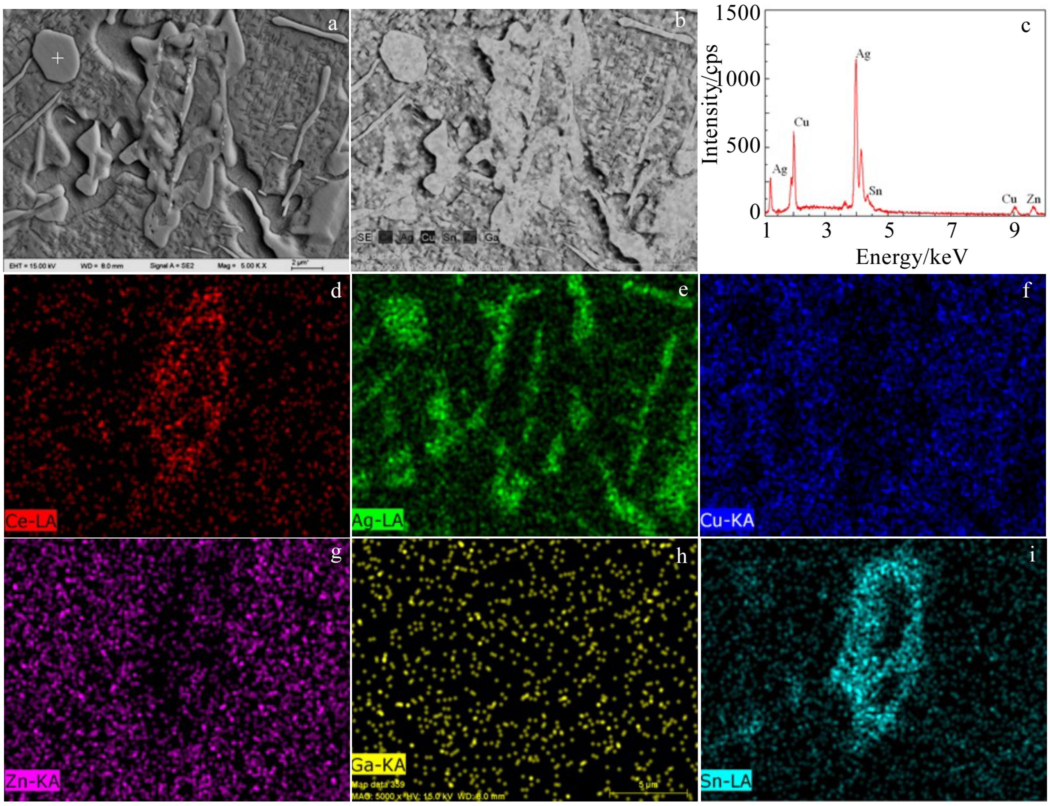

Fig.6 SEM image (a, b) and EDS mapping of Ag17CuZnSn-6Ga-0.5Ce filler alloy; (c) EDS spectrum of selected region "+" in Fig.6a; and corresponding the elements mapping: (d) Ce, (e) Ag , (f) Cu, (g) Zn, (h) Ga, and (i) Sn

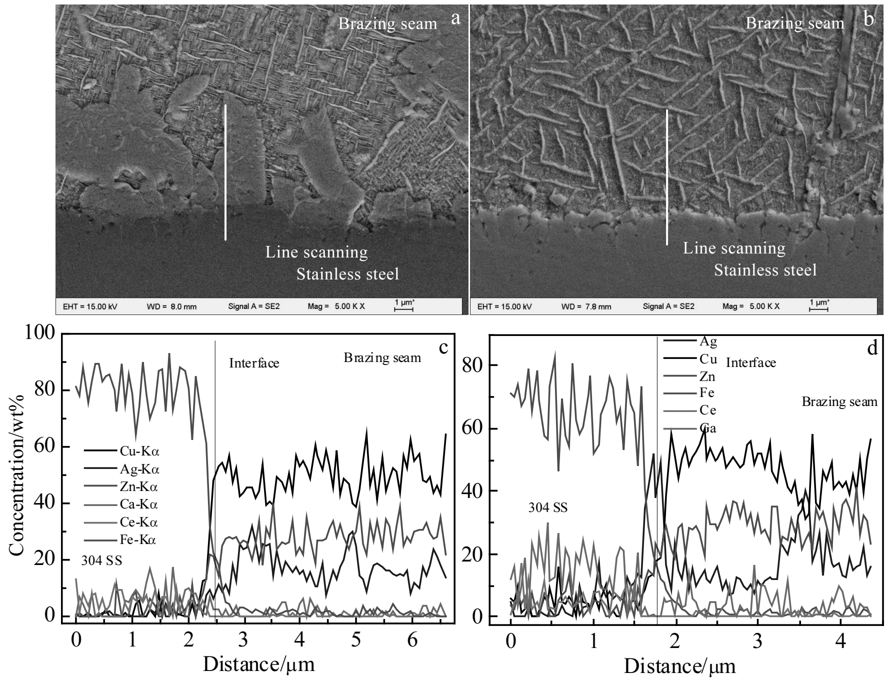

Fig.7 SEM microstructures (a, b) and their marked position element distributions (c, d) of brazed joint with different Ce and Ga contents: (a, c) Ag17CuZnSn-2Ga-0.15Ce and (b, d) Ag17CuZnSn-6Ga-0.5Ce

strength of brazed joint degenerates with further increasing of Ga and Ce content.

The shear strength of brazed joint using Ag17CuZnSn-2Ga-0.3Ce is even lower than that of Ag17CuZnSn-1Ga-0.1Ce. Fig.9 shows the fracture morphology of brazed joints. Most of fracture occurred in the interface layer between the brazing seam and 304 stainless steel. It is indicated that the interface connection is the weakest place which causes the fracture at the interface. For the Ag17CuZnSn-2Ga-0.15Ce brazed joint, the fracture surface exhibits the much finer and uniform dimples structure, as shown in Fig.9a. When the content of Ga and Ce reaches 6 wt% and 0.5 wt%, the brittle Ce-riched phases are found in Fig.9b, which deteriorate the mechanical properties of the brazed joint.

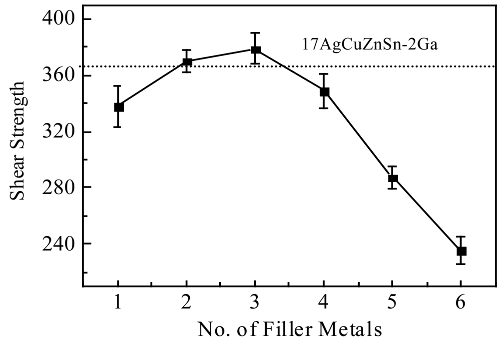

Fig.8 Shear strengths of the brazed joints using Ag17CuZnSn-*x*Ga-*y*Ce

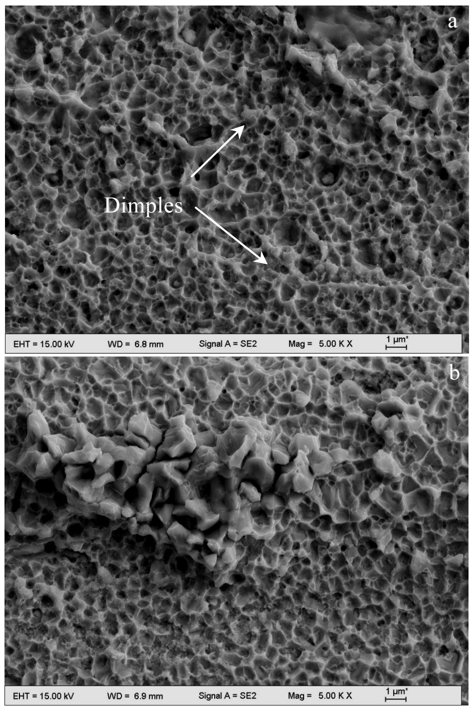

Fig.9 SEM fracture morphologies of the brazed joint with different Ce and Ga contents: (a) Ag17CuZnSn-2Ga-0.15-Ce and (b) Ag17CuZnSn-6Ga-0.5Ce

3 Conclusions

1) The solidus and liquidus temperatures decrease with addition of Ga and Ce in the filler metals. And the wettability of Ag17CuZnSn-*x*Ga-*y*Ce filler metals is significantly improved when the content of Ga and Ce are 2 wt% and 0.15 wt%, respectively.

2) The microstructure of Ag17CuZnSn-2Ga-*y*Ce filler metals becomes finer when the content range is 0.1 wt%~0.15wt%. Moreover, a novel bright $Ce_{20}(Ag,Cu)_{40}Sn_{40}$ intermetallic phase appears in the filler metal when the content of Ga and Ce are 6 wt% and 0.5 wt%, respectively.

3) During the brazing process, element diffusion is found. Ga has a higher diffusion coefficient into stainless steel than Ag, Cu, Zn and Ce. And the grain boundary permeation is found around the interface between brazing seam and stainless steel.

4) The largest shear strength of brass and stainless steel brazed joint is obtained when using Ag17CuZnSn-2Ga-0.15Ce brazing filler metal. And the fracture morphology shows numerous small and uniform dimples. However, the average shear strength of brazed joint decreases when the content of Ce is higher than 0.15 wt%.

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Ga 和 Ce 复合添加对低银无镉钎料组织及性能的影响

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摘　要：通过向 Ag17CuZnSn 钎料中复合添加微量的 Ga 和稀土元素 Ce，研究了 Ga 和 Ce 元素的复合添加对低银无镉钎料组织及焊接性能的影响。采用火焰钎焊方法得到黄铜与不锈钢异种金属钎焊接头。试验表明，随着 Ga 和 Ce 元素的添加低银钎料的固液相线温度不断下降。当 Ga 和 Ce 含量分别为 2%和 0.15%(质量分数)时，钎料在母材表面的铺展面达到最大值。Ga 和 Ce 元素的复合添加对低银钎料中的 CuZn 化合物相有明显的细化作用，黄铜与不锈钢钎焊接头的抗剪强度最大值为 378.6 MPa。在钎焊过程中，钎缝与不锈钢母材之间发生了明显的元素扩散，Ga 元素的扩散率大于其他元素。同时当低银钎料中的 Ce 元素含量大于 0.3%时，钎料组织中出现了新生成的块状稀土相。

关键词：低银钎料；显微组织；稀土元素；抗剪强度

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