Study on Preparation and Characterization of In-Ag Solders

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Abstract: A series of InAg solders were prepared by the high frequency induction melting method. Their components and phase analysis were conducted via chemical analysis and X-ray diffraction(XRD). Their melting point and surface morphology of brazing joint were characterized via differential scanning calorimeter(DSC) and scanning electron microscope(SEM), respectively. The effect of Ag addition on thermal property, joint shear strength and wettability of indium based solder alloys were investigated. The interfacial reactions of In-7Ag solder and the substrate were observed and discussed. Results showed that the addition of Ag improved both the melting point and joint shear strength of the solder alloys. In-7Ag has demonstrated large shear strength and appropriate wettability, which has a great potential to be the solder for the retrieving lunar sample container. Excessive interaction between solder and substrate for the improper temperature and time of brazing process, which will weaken homogeneity of the metallic seal. Therefore, the appropriate temperature and time of InAg solder must be founded in the future research.
Key words: metal materilas; InAg solder; the melting point; wettability; joint shear strength; interfacial reactions
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铟银软钎料的制备与钎焊性研究

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摘　要：用感应熔炼方法制备了一系列 InAg 钎料，考察银添加量对铟基钎料性能的影响。采用化学分析和 X 射线衍射(XRD)对钎料的成分和物相进行了对比分析；采用示差扫描量热仪(DSC)测试了不同成分钎料的熔点；利用扫描电镜(SEM)对 In-7Ag 焊料与基体的界面反应进行了研究，并测试了不同成分钎料的润湿性及接头剪切强度。结果表明，In-7Ag 具有较大的剪切强度以及良好的润湿性，是月球样品返回装置密封材料的不错选择。焊料与密封材料剧烈反应可能弱化焊接组织的一致性，不利于金属密封，因此，寻求合适的焊接温度和时间是未来研究的重点。
关键词：金属材料；铟银钎料；熔点；润湿性；接头强度；界面反应

Indium is widely applied in brazing non-metal material such as glass, quartz and ceramic，due to its low melting point (156.6℃) and excellent brazing property. The brazing of the optical cover and glass window is very important in order to meet the vacuum requirements of the MOEMS. Indium and indium based alloys are widely used in metal sealing as they feature low vapor pressure, fine plasticity and work unhardening which largely deform under a little stress[1]. Indium based solder has low elastic strength

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and it can effectively absorb the stress formed in the process of the seal brazing and thermal stress in subsequent thermal cycle of cover body and glass window to avoid the cracks on the interface of brazing which could lead to seal failure, and Indium can form intermetallic compounds with good ductility which helps to ensure the reliability of expensive and advanced optical systems to serve a long-term goal[2]. For night vision devices and other applications, the transmission-mode photocathodes must be sealed into tube by indium seal process in practical application[3]. According to the sealing requirement of the retrieving lunar sample container, we have designed a seal structure which blade squeezed into soft indium metal. The interconnection requires that indium solder is brazed into the sealing groove of the device's lid in the earth's lab first, and then under the condition of the moon surface, the lid of the sample container is tightened by the locking mechanism of the device which enables the blade to squeeze into seal indium to form seal eventually[4]. For the structure, indium is used not only as the solder which is welded in the lid but also as sealing metal for the container.

Duo to its low joint strength, pure indium could not meet the requirements of high strength brazing joint. The addition of alloying elements, e.g. Ag, Al, Co, Ga, Ge, In, Ni, Sb, Ti, Zn into a solder is a useful method to improve the physical properties of the solder. Although these elements could improve certain properties of the solder, they could undesirably alter some properties of the alloy, and the alloying elements react variedly to different solder alloys[5]. Sliver has been used as an alloying element in solder alloys due to its relatively low cost and several other beneficial properties. In order to improve the properties of indium solders, a great deal of efforts have been conducted. The addition of Ag can be an effective approach to improve the properties of indium solders. Thus in this paper, we apply this comparative research method on In-Ag alloy solders with different silver content, which aimed to investigate the effect of Ag alloying element on the improvement of In based solders with respect to thermal behavior, wettability and properties of brazing joint. The resulting microstructure of the brazing seam formed at the interface between solder and substrate were also investigated. The research results will help to develop In-Ag alloy solder for the moon exploration project in the future. Fig.1 is the phase diagram of In-Ag alloys.

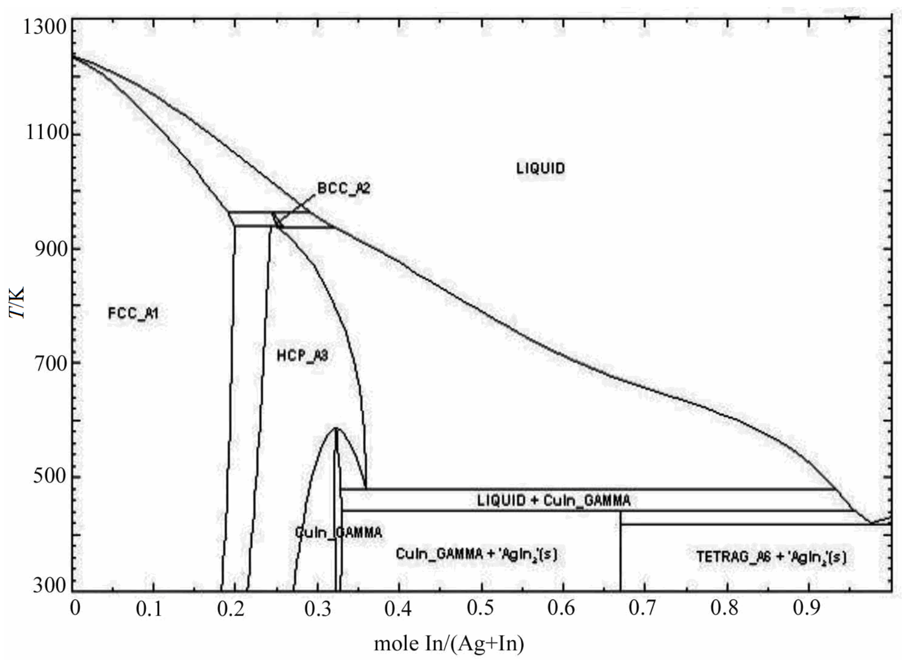

Fig.1 The phase diagram of In-Ag alloys 图 1 In-Ag 二元合金相图

1　Experiment

In order to carry out comparative research on InAg solders, a series of InAg solders were prepared. The ingots were weighed and melted in an electromagnetic induction quartz tube under vacuum to prevent the alloys from oxidation, followed by natural cooling in vacuum. All the solders were re-melted twice to achieve high homogeneity and assure the same amount of each piece of alloys in the experiment. The components and phases of InAg ingoting were analyzed with chemical analysis and XRD. Thermal properties of In-Ag solder alloys were investigated by differential scanning calorimetry. The scanning temperature started from 50 to 250°C and heating rate at a same rate of 3°C/min. The test was performed under argon atmosphere. The wettability was evaluated by wetting angle. The results reported in this paper were the average values of at least three tests. The microstructures and chemical compositions of interfacial metallic compounds (IMCs) were characterized using a scanning electron microscope with an energy dispersive X-ray spectroscope (EDX).

2　Results and discussion

2.1　Characterization of indium silver solder

The detailed sample composition and silver content in different positions are shown as Tab.1. Silver content increases from the top to bottom of ingot casting. The cause of un-uniformity in chemical composition of ingot casting is that silver melting point is 961°C, which is far higher than the melting temperature of indium(156.6°C), so indium melts first and floats on the silver surface. As it is further heated, silver melts completely. Due to its low density indium clusters at the top of ingot casting while liquid silver with high density clusters at the bottom.

The chemical analysis and XRD results shown above are representatives for samples' chemical composition and crystallography examination, and results in general are similar and repeatable for different examined ingots. In conclusion, In-Ag ingots of nearly homogeneous and polycrystalline have been successfully prepared by using re-melted twice casting method. As shown in Fig.1, all of the samples have similar diffraction pattern and diffraction peak which demonstrates that they have the same phase and are made up of two phases of In and In-Ag_2[6].

Tab.1 Mass fraction of Ag in No.1~No.4 alloy

表 1 No.1#~No.4#合金中因的质量分数　/%

Sample	1#	2#	3#	4#
Content	3.00	5.00	7.00	9.00
Top	2.87	4.87	7.01	9.88
Middle	3.09	4.92	7.13	10.03
Bottom	3.03	5.07	7.14	10.11
Average	3.00	4.95	7.09	10.01

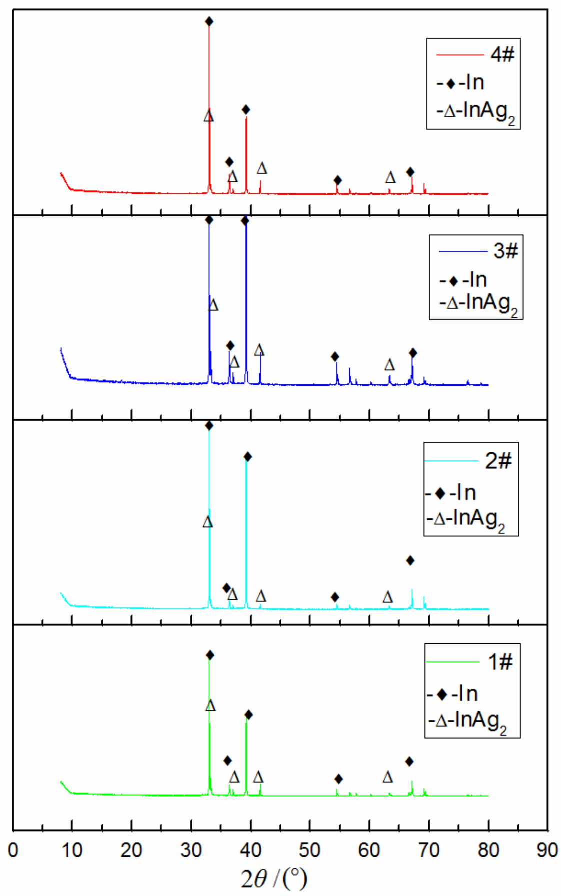

Fig.2 XRD of In-Ag Alloys　图 2　铟银合金 XRD 图谱

2.2　Thermal and wettability analysis

The melting point and wettability of four solders were tested in the experiment. Indium melting temperature is 156.6℃ which has been measured in previous study. As shown in Tab.2.

Tab.2 Melting point, wetting angle and strength of designed In-Ag alloys

表 2 In-Ag 合金试样熔点、润湿角及强度

Sample	1#	2#	3#	4#
Melting point/°C	144.2	159.7	164.5	172.4
Wetting angle/(°)	8	15	18	20
Strength/MPa	0.56	1.87	5.30	9.86

The melting temperature of InAg alloys increase with Ag addition. The increase of the melting point is attributed to the presence of Ag, which has a higher melting point and excellent wettability. In-Ag solder melting temperature increases from 144.2 to 172.4°C when Ag content is from 3% to 9%. Thu, the solder of certain melting point can be prepared by controlling the Ag amount to meet the requirements of different brazing. Therefore, the results of thermal analysis indicate that In-Ag alloys are acceptable and have a great potential to be the solder of retrieving lunar sample container as low-temperature lead-free solders. Generally, the reflow temperature is about 20~40°C higher than the melting point of solders. A lower melting point thus leads to a lower reflow temperature, which is desirable because the risk of thermal damage or warpage of certain base metal. A lower melting temperature also means that there would be no demand for the soldering processes. Under the condition of specified brazing temperature, the liquid solder flows into the brazing seam and the interface between base metals involved, and then the as-cast brazing joint is formed when the liquid solder solidifies[7,8]. The essential condition of liquid solder filling into the brazing seam is that liquid solder can smoothly wet and spread on the surface of base metal[7].The solder shows good wettability when there is mutual interaction and stimulation among elements of solder and base metal. However, if the mutual interaction and stimulation is too violent, solder wettability reduces because of the heavily interaction between liquid filler metal and the base metal resulting in the increases of solder viscosity and melting point preventing liquid solder from fully spreading on the surface[4]. Solder shows good wettability and spreading effect only under proper interaction with the base metal.

In the experiment, silver layer with a thickness of about 10 μm is electroplated first, which is prepared to improve the solder's surface and spreading of In-Ag alloy and base metal of 7570Al and protect the base metal from corrosion, but it makes its components and characteristics of brazing joint more complex. It is known that a small value of wetting angle corresponds to a better wettability. Tab.2 depicts the wetting angles of In-Ag solder alloys after soldering at 215℃. As shown, when the brazing temperature is identical and constant, the wetting angles increased significantly with Ag mass fraction from 3% to 9%. When the Ag content reached 9%, the wetting angle was 20°, revealing that the content of Ag added should be effectively controlled to insure the wettability of In-Ag solder. It is mainly because Ag addition which has a higher melting point than indium's increase viscosity and melting temperature of liquid solder, which will prevent liquid solder from fully spreading on the surface of the base metal. Composition of 7075 alloy is shown in Tab.3

Tab.3 Chemical composition of 7075 alloy

表 3 7075 合金的化学成分

Element	Si	Fe	Cu	Mn
ω/%	0.15	0.4~0.45	1.3~1.5	0.1
Element	Cr	Ti	Mg	Zn
ω/%	0.2~0.24	0.03~0.05	2.6~2.8	5.5~5.8

2.3 Shear strength of brazing joint

The shear strength of brazing joint is one of the most important mechanical performance indicators of a solder. In practical applications, solder joint is mainly under shear stress which is always less than its tensile strength. Therefore, solder joints with different Ag content have been tested to check their shear strength in the experiment. As shown in Tab.2, the observation based on the shear test experiment in indium silver solid solution system is normal to solid solution strengthening theory. The shear strength of joints increases with Ag content. The shear strength of solder joint of 3% Ag is too low for the seal structure of the lunar sample container, because it mainly composes of In which belongs to the soft metal enduring small shear strength. When Ag increased up to 7%, the shearing strength of joint comes to significant improvement which can bears certain shear strength of lunar sample container.

2.4 Characterization of In-7Ag brazing joint

Based on the preliminary study of thermal properties, wettability and the mechanical properties, the In-7Ag solder is a promising candidate for interconnection applications in seal structure of the lunar sample container. Further research, the microstructures and chemical compositions of interfacial metallic compounds were characterized using SED. Fig.3 shows the microstructure of the interface between In-7Ag solder and Al substrate after soldering.

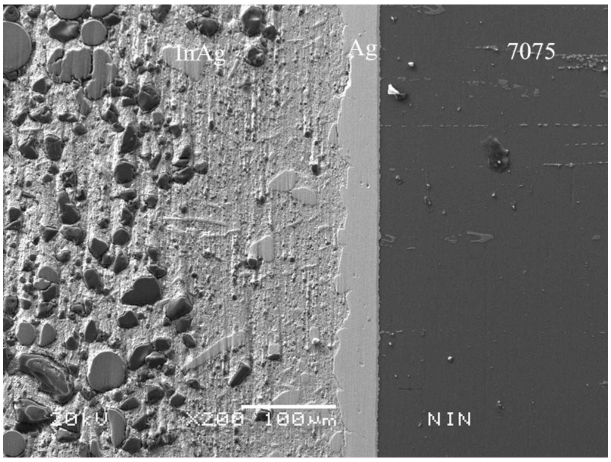

Fig.3 The SEM image of In-7Ag welded joint

图 3 In-7Ag 焊接接头的 SEM 图像

Typically, as predicted in brazing theory, liquid solder interacts with solid base metal in brazing process which is derived from the diffusion of concentration gradient[9]. The interaction can be divided into two types, the base metal dissolves in the liquid solder and the liquid solder diffuses in the base metal, which has great influence on the performance of the brazing joint[10]. Meanwhile, the brazing process can be improved and adjusted accordingly. As brazing joint SEM shows in Fig.3, It can be seen that the addition of Ag slightly influence on the morphology. The silver layer which reaches 30 μm has obvious extension compared to before. The energy spectrum analysis of the silver layer shows that the IMCs formed between In-7Ag solder and Al substrate was identified as In–Ag layer due to the liquid solder diffuses in the Ag layer and formed InAg intermetallic compounds which improve the joint strength. The spectrum analysis shows that the composition and microstructure of the base metal of 7075Al remains unaffected by the diffusion of solder elements. It is mainly because that Al and In cannot react to form solid solution or intermetallic compounds[11]. Al, Mg, Zn, Cu of substrate dissolved is found in the solder side. A certain amount of solution of base metal will improve the microstructure of the brazing seam components and enhance strength of the brazing joint by alloying effect. However, excessive solution of Al, Mg and Zn may deteriorate the consistency of seal material hardness, which has adverse impact on seal of the lunar sample container. As described above, the appropriate temperature and time of brazing process must be defined, which became the next study of future research.

3 Conclusion

In the paper, the materials of indium silver solid have been grown in the ingot form two phases of In and In-Ag_2. The effect of sliver addition on the improvement of Indium based alloy solder was investigated, with respect to the thermal properties, wettability, the mechanical properties.

1) The solders with a certain melting temperature can be prepared by controlling the Ag content to meet the requirements of different brazing.

2) The In-7Ag solder have demonstrated the large shear strength which can bears certain shear strength and appropriate wettability, which has a great potential to be the solder of the lunar sample container.

3) As we have known, excessive interaction between solder and substrate for the improper temperature and time of brazing process, which will weaken homogeneity of the metallic seal. Therefore, the next study is to optimize appropriate the

temperature and time of brazing process.

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