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ARTICLE

Effect of Rare Earth Pr on Creep Behavior of Sn-0.3Ag-0.7Cu-0.5Ga Low-Ag Solder Alloys

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Abstract: For development of low-Ag lead free solder alloys for microelectronic packaging, the correlation of creep properties with microstructure of novel Sn-0.3Ag-0.7Cu-0.5Ga (SAC-Ga) solder alloys bearing Pr has been investigated using nanoindentation. The results show that the creep deformation of SAC-Ga, SAC-Ga-0.06Pr, SAC-Ga-0.5Pr is 1717, 1144, and 1472 nm, respectively, which indicates that Pr addition could significantly enhance the creep resistance of SAC-Ga solders due to the refinement and uniform distribution of Cu_6Sn_5 intermetallic compounds (IMCs). However, compared with the SAC-Ga-0.06Pr solder alloy, the SAC-Ga-0.5Pr alloy shows poorer creep resistance which is mainly attributed to the surface oxidation of excess rare earth Pr. In addition, Dorn model has been used to describe the creep behavior and to obtain stress exponents of the SAC-Ga solder alloys bearing Pr. The strengthening mechanism of creep resistance in SAC-Ga solder alloys bearing Pr is that when encountering refined and well-distributed Cu_6Sn_5 IMCs, a dislocation line cannot climb through the IMCs but bypass the IMCs, thus leading to a decrease in the creep deformation of the solder alloys bearing Pr.

Key words: rare earth Pr; Sn-Ag-Cu-Ga solder; creep behavior; microstructure

As waste electrical and electronic equipment (WEEE) legislation[1] and restriction of the use of certain hazardous substances (RoHS) legislation[2] have been implemented in Europe, application of traditional Pb filler metals of solder are restricted. Among all the lead-free solders, Sn-Ag-Cu high-Ag solders, in which the Ag content is usually higher that 3.0%, are considered to be the most promising substitutes due to their low available melting temperature, near-eutectic composition, and favorable thermal-mechanical fatigue properties[3]. However, some problems of the existing high-Ag solders cannot be avoided, such as inferior drop impact reliability and high cost[4]. Therefore, it is imperative to develop and research new Sn-Ag-Cu low-Ag solders (ω(Ag)≤1%), such as SAC0307, not only for cost but also mechanical factors.

With reducing Ag content, the solder alloys are more ductile and compliant solders for high impact conditions which can offer a better resistance to drop failure in the interconnections[5]. Compared with commonly used Sn-3.8Ag-0.7Cu high-Ag alloy, however, Sn-Ag-Cu low-Ag solders show slightly higher melting point[4], larger melting range[6], poor creep and thermal fatigue performance[7], which are major restricts in promoting the use of Sn-Ag-Cu low-Ag solders in the electronics industry. How to enhance the creep resistance of Sn-Ag-Cu low-Ag solders can barely be seen in the literature reports[8,9]. Gao et al[10] reported that adding rare earth Pr can improve the mechanical properties of Sn-Ag-Cu solder joints and Zhang et al[11] reported that the addition of Ga can optimize the microstructure and the oxidation resistance of Sn-Ag-Cu solders. So based on that adding trace amount of Ga can get an optimal Sn-Ag-Cu microstructure, this paper

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investigates the effect of Pr on the creep resistance of Sn-0.3Ag-0.7Cu-0.5Ga (SAC-Ga) solder.

As is known to all, creep behavior of metallic materials can be characterized by many different kinds of test methods. However, with regard to microelectronic packaging industry, with the miniaturizing trend of electronic devices, the size of solder joint usually reached a level below the millimeter scale, which brought size effect for the mechanical properties of solder joint[12]. Consequently, traditional tensile and shear creep test methods could not well reflect the actual creep behavior of newly solder joint in its service. Pleasantly, hardness, modulus and other mechanical parameters could be got under the premise of not damaging the material through the nanoindentation *P-h* curve[13]. Naturally, it had been widely used in the mechanical performance testing of the materials with a small size. Nanoindentation could not only ensure the test area to have the characteristics of precise location and small size, but also continuously record the changes of depth and load during the process of indentation, which provided a great convenience for the study of the mechanical properties of the material with a micro-size.

Thus, the objective of this work is to investigate the effect of Pr on the creep behavior of SAC-Ga solders. The indentation depths and creep stress exponent *n* have been studied by the nanoindentation *P-h* curve. Furthermore, the mechanism of Pr on the creep behavior has been also understood.

1 Experiment

Pure Sn, Ag, Cu and Ga with purity of 99.95 wt% were used as raw materials. Rare earth Pr with purity of 99.5 wt% was used to react with Sn and form Sn-5Pr alloy ingots. The Sn-5Pr alloy, Sn, Ag and Cu were melted at 900±10 °C in a vacuum furnace to fabricate SnAgCuPr alloy. The molten alloy was held for 4 h while mechanical stirring was performed every 30 min using a stainless steel rod to homogenize the alloy. Next step was to control the melt temperature below 400 °C and then 0.5 wt% of pure Ga was added into the melt. After about 5 min of heat preservation and mechanical stirring which was performed every 1 min, the melted solder was chilled to cast and the ingot was cut into tin bars with about 40 mm in length. The composition of solder alloys was analyzed by the inductively coupled plasma emission spectrometer (ICPAES) and is listed in Table 1.

Table 1 Nominal and actual chemical composition of the solder alloys (wt%)

Solder alloys	Ag	Cu	Ga	Pr		Sn
				Nominal	Actual	
a	0.3	0.7	0.5	0	0	Bal.
b	0.3	0.7	0.5	0.06	0.058	Bal.
c	0.3	0.7	0.5	0.5	0.52	Bal.

Nanoindentation tests were accomplished by a Shimadzu® DUH-W201 dynamic ultra microhardness tester equipped with a Berkovich (trigonal) diamond tip nanoindenter. The nanoindentation was performed by driving the indenter at a constant loading rate of 1 mN/s into the samples' surface with the maximum applied load of 50 mN, and then it was held for 5 min at room temperature (298 K). In order to ensure the accuracy of results, the test of each sample was conducted five times and the average value was taken as the final result.

2 Results and Discussion

2.1 Analysis of creep equation for nanoindentation

Fig.1 shows the melting point of SAC-Ga solder is 213 ºC. At room temperature, the specific temperature value is still more than 0.3 times of the melting point of SAC-Ga solder. Working at room temperature, creep is one of the most important deformations. Fig.2 shows the typical creep curve of solders, from which we can see that under constant stress the creep is subjected to three stages, including primary creep (decelerated creep), secondary creep (steady state creep) and tertiary creep (accelerated creep). The deformation of secondary creep is easy to calculate so that its creep speed is usually used as a measurement of creep resistance of vast majority materials. The equation used in this paper on describing secondary creep is Dorn equation[14].

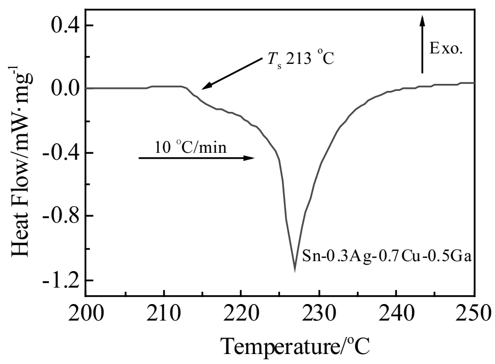

Fig.1 DSC curve of the SAC-Ga solder alloy

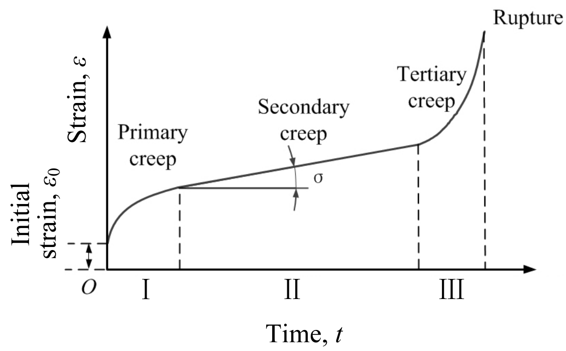

Fig.2 Typical creep curve of solders

$$\dot{\varepsilon} = A_1 D_0 \frac{Gb}{RT}\left(\frac{b}{d}\right)^p \left(\frac{\sigma}{G}\right)^n \exp\left(\frac{-Q}{RT}\right) \tag{1}$$

where A_1 is the material parameter, D_0 is self-diffusion coefficient, G is shear modulus, b is Burgers, d is interplanar spacing, σ is yield strength, n is stress exponent, R is gas constant, T is absolute temperature, and Q is activation energy of diffusion.

Eq. (1) can be further simplified as

$$\dot{\varepsilon} = B\sigma^n \exp\left(\frac{-Q}{RT}\right) \tag{2}$$

It is not easy to determine the stress and strain of the material under the condition of nanoindentation test. Comparatively, the hardness of the material (H) will be much easier to obtain. Under the condition of a certain temperature and working hardening ability, H is a function of strain rate. Therefore, in the nanoindentation test the creep behavior can be expressed as:

$$\dot{\varepsilon} = C(H)^n \tag{3}$$

Creep deformation mechanism is mostly identified by the value of the stress exponent n. In the process of nanoindentation test, creep behavior is related to the diffusion rate from the plastic zone boundary to the internal of the material. Generally, the ratio of instantaneous contact area change rate to the area ($\dot{S}/S$) is defined as the indentation strain rate $\dot{\varepsilon}$.

A Berkovich indenter tip is a three-sided pyramid which is geometrically self-similar and has the same projected area-to-depth ratio as a Vichers indenter. So under the assistance of the Berkovich indenter, ($\dot{S}/S$) can be expressed as the ratio of instantaneous indentation depth rate to the depth ($\dot{h}/h$). Considering that SAC-Ga solders can be regarded as perfect plastic materials, the current indentation depth is equal to the depth of plastic deformation. And the instantaneous indentation depth rate is:

$$\dot{h} = \frac{dh}{dt} \tag{4}$$

In the process of nanoindentation test, the hardness of the material is defined as:

$$H = \frac{P}{S} \tag{5}$$

where P is instantaneous load and S is the projected area of the indenter. In this experiment, S of the Berkovich indenter is:

$$S = 24.56h^2 \tag{6}$$

Take Eq. (4) and Eq. (5) into Eq. (3), can be expressed as:

$$\frac{dh}{dt}\frac{1}{h} = C\left(\frac{P}{S}\right)^n \tag{7}$$

Then take the natural logarithm on both sides of Eq. (7):

$$\ln\left(\frac{dh}{dt}\frac{1}{h}\right) = \ln C + n\ln\left(\frac{P}{S}\right) \tag{8}$$

The stress exponent n can be written as:

$$n = \frac{\partial \ln(\dot{h}/h)}{\partial \ln(P/S)} = \frac{\partial \ln\dot{\varepsilon}}{\partial \ln H} \tag{9}$$

The creep stress exponent n of the solder can be obtained from Eq. (9). However, the creep indentation may have fluctuation due to the undulation of the sample surface roughness and the environmental conditions. In particular, at the last stage of creep deformation, the strain rate is very low, and it will bring larger error if the measurement data of dh/dt is used directly for calculating the creep stress exponent n. The data needs appropriate treatment, including removal of the invalid data points obtained at the last stage of creep and using the graphing method and linear fitting method to determine the stress factor n.

2.2 Creep stress exponent *n* of SAC-Ga-*x*Pr solders

Fig.3 shows the P-h curves of the SAC-Ga-xPr (x=0, 0.06, 0.5) solders at room temperature. The maximum load of 50 mN is kept for 5 min in order to achieve the steady state creep. The indentation depths of SAC-Ga, SAC-Ga-0.06Pr, SAC-Ga-0.5Pr solders are 5475, 4591 and 4905 nm, respectively. Solders with varied components show obvious differences in the indentation depths, and the base solder SAC-Ga has the maximum depth, which indicates that the addition of Pr can improve the creep resistance of SAC-Ga solder.

During the process of maintaining the maximum load, an obvious creep behavior occurs in the solder. In order to observe the steady state creep behavior of different solders in detail and to increase the contrast effect of data, the depth-time curve of the secondary creep is drawn in Fig.4, and the horizontal and vertical coordinate values of the origin of the curve are adjusted to zero. As can be seen from Fig.4, with the increasing of the time, the rate of increase in creep deformation gradually decreases, and after keeping maximum load for about 300 s, the deformation of three solders reaches 1717, 1144 and 1472 nm. SAC-Ga solders bearing Pr show better creep resistance and the one with 0.06 wt% Pr addition exhibits the minimum creep deformation.

Furthermore, the data of points in h-t curve (Fig.4) has been used to calculate the creep stress exponent n through a linear fitting method according to Eq.(9). $\ln\dot{\varepsilon}$-ln$H$ curve has been drawn and the slope of the curve is the creep stress exponent n. As shown in Fig.5, n of SAC-Ga, SAC-Ga-0.06Pr and SAC-Ga-0.5Pr are 4.48, 6.19 and 5.53, respectively. It suggests that the SAC-Ga-0.06Pr solder has the maximum creep stress exponent n, and it indicates that SAC-Ga-0.06Pr solder has the best creep resistance.

Under the condition of a certain load, creep can be divided into three types according to the ratio of test temperature (T) to the melting point (T_m) of the material. They are low temperature creep ($T<0.25T_m$), medium temperature creep ($T=0.25\sim0.5T_m$) and high temperature creep ($T>0.5T_m$). The room temperature (298 K) is much more than 0.5 times of the melting temperature of SAC-Ga solder (approximately

494 K). Obviously, SAC-Ga solder joints exhibit features of high temperature creep. Under these circumstances, dislocation slipping, climbing and thermal diffusion will take place in the solder. If the temperature and stress is high enough, the movements of dislocations will increase and dislocation climbing is the major control mechanism of creep behavior. By consulting Ref.[15,16], the creep stress exponent n is 3~20, and from these researches the major mechanism of solder's creep behavior can be determined as dislocation climbing. As can be seen from Fig.6, appropriate addition of Pr can optimize the microstructure of solders and morphology of IMCs, which increases the resistance for dislocation climbing.

Because of the limitation of the equipment condition, the creep activation energy Q has not been deduced. However, according to Eq. (7), it does not affect the evaluation of solders' creep resistance.

2.3 Strengthening mechanism for SAC-Ga-*x*Pr solders

According to the Orowan mechanism[17,18], when a dislocation line meets the undeformable reinforced particles, the repulsive stress is large enough so that the dislocation line will bend before the particles (Fig.7). The critical stress that the dislocation line could exactly bypass the particles is called Orowan stress.

$$\tau_0 = \frac{Gb}{\lambda} \approx \alpha f^{\frac{1}{2}} r^{-1} \tag{10}$$

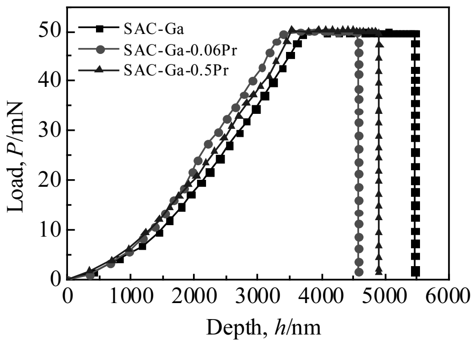

Fig.3 *P-h* curves of Sn-0.3Ag-0.7Cu-0.5Ga-*x*Pr solder

where constant α is 0.093 for edge dislocations and 0.14 for screw dislocations, f and r are the volume fraction and average radius of the particle, respectively. Obviously, the greater the density of particles and the smaller the radius are, the more obvious the strengthening effect.

Similarly, although the stress for creep is lower than that of Orowan stress, the effect of dispersing phases in the dislocation climbing is almost identical with only minor differences. As the solid solubility of Ag and Cu in the solder is very little, it does not affect the mechanical behavior in a form of solid solution. Moreover, though Ga solutes in the Sn matrix, the content of Ga is very little and it will react with Ag and Cu which decreases the solution in Sn matrix.

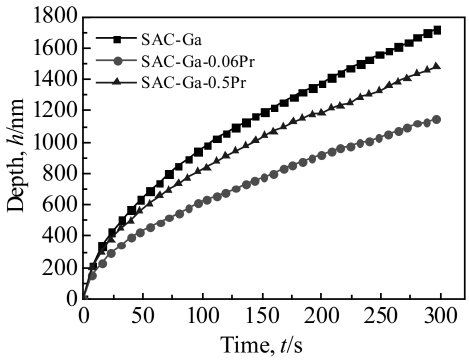

Fig.4 *h-t* curves of Sn-0.3Ag-0.7Cu-0.5Ga-*x*Pr solder

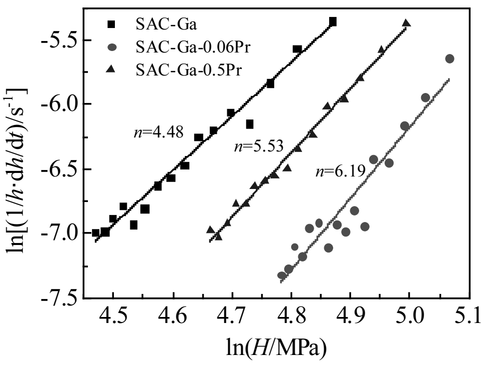

Fig.5 Creep stress exponent n of Sn-0.3Ag-0.7Cu-0.5Ga-*x*Pr solder

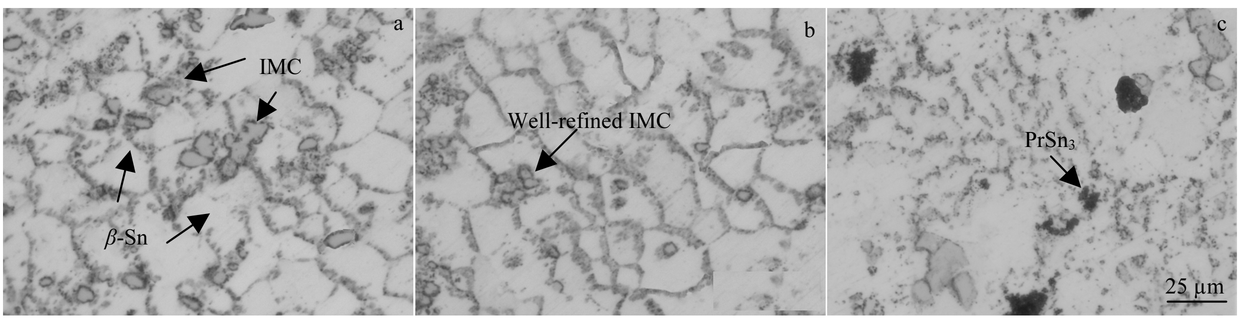

Fig.6 Microstructures of SAC-Ga-*x*Pr solders: (a) 0 Pr, (b) 0.06 Pr, and (c) 0.5 Pr

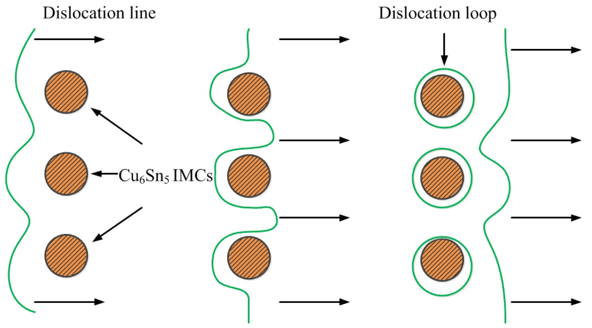

Fig.7 Schematic diagram for the Orowan mechanism

Thus, the effect of Ga solution on mechanical behavior is only a little too. Critically, the existing form of Ag and Cu in solder is the IMC. The morphology, distribution and size of IMCs have a significant effect on the mechanical behavior of the solders. The deformation resistance of IMC is much higher than that of Sn matrix, and dislocations cannot climb through the IMC. Consequently, the dislocations will bypass the IMC just like the Orowan mechanism. Huang et al[19] complements that the creep resistance of Sn-based solder is mainly due to the volume fraction of strengthening particles. Synchronously, creep resistance gets better with the increasing of volume fraction of IMCs.

The microstructure of SAC-Ga solders can be refined and homogenized by adding a trace amount of Pr (Fig.6). Moreover, the size and existing form of IMC can be also ameliorated, which disperses in the Sn matrix. In this paper, the refinement and homogenization of IMC particles by adding 0.06wt% Pr is thought to be responsible for the improving of creep resistance. And the content of Ag_3Sn is little, and thus the strengthening effect is considered to be mainly from Cu_6Sn_5 phases (Fig.8). However, $PrSn_3$ phases will arise if excess Pr is added (Fig.9), which is rapidly oxidized and microcrack will appear in the surface after oxidation. And what is worse is that needle-like structure arises in the morphology of solders, which leads to the decline of strengthening effect of IMCs, and consequently the creep resistance decreases.

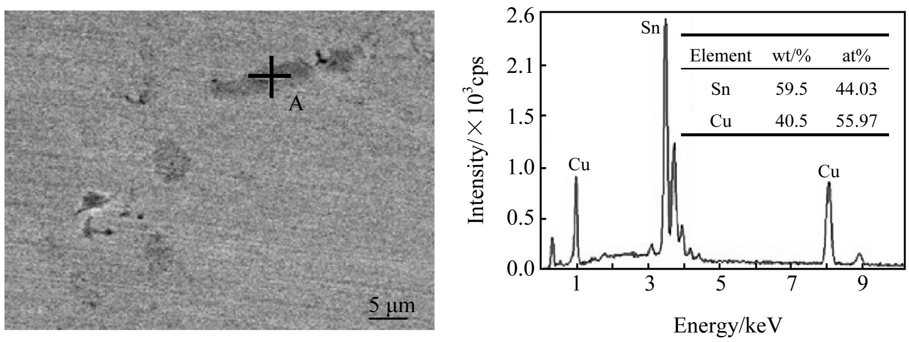

Fig.8 EDX analysis of Cu_6Sn_5 phase

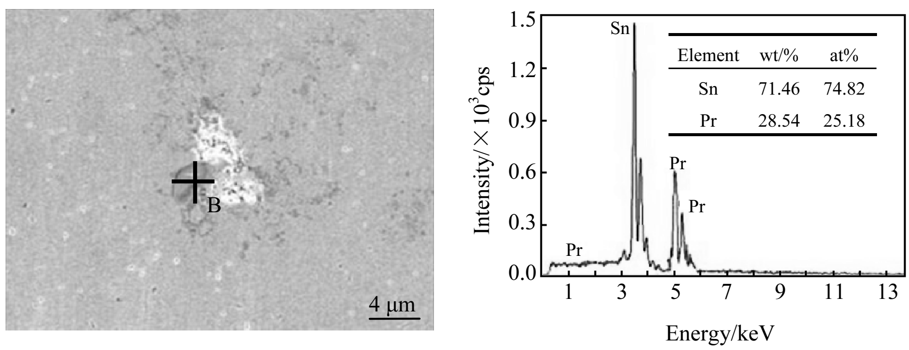

Fig.9 EDX analysis of $PrSn_3$ phase

3 Conclusions

1) Creep equation for nanoindentation has been analyzed and the creep stress exponent n of SAC-Ga, SAC-Ga-0.06Pr and SAC-Ga-0.5Pr is 4.48, 6.19 and 5.53, respectively, which means n can be significantly improved by adding an appropriate amount of Pr. And the optimal addition of Pr in this paper is 0.06 wt%.

2) The increasing of creep stress exponent n means the improving of creep resistance, which depends on the optimization of IMCs in the solder's microstructure. Dislocations cannot climb through IMC particles, which is similar to the Orowan

mechanism. The addition of Pr evidently ameliorates the distribution of IMC. However, with an excessive amount of Pr addition, the formation of needle-like brittle Pr-rich IMCs deteriorates the creep resistance.

References

1 Salhofer S, Steuer B, Ramusch R *et al*. *Waste Management*[J], 2016, 57: 27

2 Zhang L, Xue S B, Gao L L *et al*. *Rare Metal Materials and Engineering*[J], 2010, 39(3): 382 (in Chinese)

3 Amin N A A M, Shnawah D A, Said S M *et al*. *Journal of Alloys and Compounds*[J], 2014, 599: 114

4 Gu Y, Zhao X C, Li Y *et al*. *Journal of Alloys and Compounds*[J], 2015, 627: 39

5 El-Daly A A, Hammad A E, Fawzy A *et al*. *Materials & Design*[J], 2013, 43: 40

6 El-Daly A A, Fawzy A, Mansour S F *et al*. *Journal of Materials Science: Materials in Electronics*[J], 2013, 24(8): 2976

7 Chuang C L, Tsao L C, Lin H K *et al*. *Materials Science and Engineering A*[J], 2012, 558: 478

8 Che F X, Zhu W H, Poh E S W *et al*. *Journal of Electronic Materials*[J], 2011, 40(3): 344

9 Hammad A E. *Materials & Design*[J], 2013, 52: 663

10 Gao L L, Xue S B, Zhang L *et al*. *Journal of Materials Science: Materials in Electronics*[J], 2010, 21(9): 910

11 Zhang Q K, Long W M, Yu X Q *et al*. *Journal of Alloys and Compounds*[J], 2015, 622: 973

12 Xu L, Pang J H L. *Journal of Electronic Materials*[J], 2006, 35 (12): 2107

13 Liu C Z, Chen J. *Materials Science and Engineering: A*[J], 2007, 448(1-2): 340

14 Mavoori H, Chin J, Vaynman S *et al*. *Journal of Electronic Materials*[J], 1997, 26(7): 783

15 Weertman J. *Journal of Applied Physics*[J], 1955, 26(10): 1213

16 Weertman J. *Journal of Applied Physics*[J], 1957, 28(3): 362

17 Peng Y Y, Yin Z M, Lei X F *et al*. *Rare Metal Materials and Engineering*[J], 2011, 40(2): 201 (in Chinese)

18 Ahlquist C N, Gascaneri R, Nix W D. *Acta Metallurgica*[J], 1970, 18(6): 663

19 Huang M L, Wu C M L, Wang L. *Journal of Electronic Materials*[J], 2005, 34(11): 1373

稀土 Pr 对低银 Sn-0.3Ag-0.7Cu-0.5Ga 钎料蠕变行为的影响

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摘　要：为进一步促进电子封装用低银无铅钎料的发展，本实验采用纳米压痕法研究了新型含 Pr 低银 Sn-0.3Ag-0.7Cu-0.5Ga (SAC-Ga) 钎料显微组织与蠕变性能之间的关系。结果表明，SAC-Ga、SAC-Ga-0.06Pr、SAC-Ga-0.5Pr 3 种钎料的蠕变位移分别为 1717，1144，1472 nm；稀土 Pr 可通过细化 Cu_6Sn_5 金属间化合物并促使其均匀分布从而明显提高 SAC-Ga 钎料的蠕变强度；与 SAC-Ga-0.06Pr 钎料相比，SAC-Ga-0.5Pr 由于过量稀土 Pr 的表面氧化而导致其蠕变强度有所下降。此外，本实验采用 Dorn 模型研究了含 Pr 的 SAC-Ga 钎料的室温蠕变行为并计算了对应的钎料蠕变应力指数 n；阐明了 Pr 对 SAC-Ga 钎料蠕变强度的强化机理，即当位错遇到细小且均匀分布的 Cu_6Sn_5 金属间化合物时，位错移动只能采用绕过机制，从而提高了含 Pr 低银钎料的抗蠕变性能。

关键词：稀土Pr；Sn-Ag-Cu-Ga钎料；蠕变行为；显微组织

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