

MINGJIANG JIN*, QIANG LI*, RENLONG YING**, XIANWEN LU*, XUEJUN JIN*, XIFAN DING***#

INTERNAL FRICTION OF PHASE TRANSFORMATIONS OBSERVED AROUND ROOM TEMPERATURE IN Ga-In-Sn EUTECTIC ALLOYS

TARCIE WEWNĘTRZNE PRZEMIAN FAZOWYCH OBSERWOWANYCH PRZY TEMPERATURZE POKOJOWEJ W EUTEKTYCZNYM STOPIE Ga-In-Sn

The phase transformation phenomena in eutectic Ga-In-Sn alloys around room temperature are studied by thermal analysis, internal friction, and in-situ XRD methods. The results show that in addition to the solidification transformation, a novel the so-called 'pre-solidification' phase transition, demonstrating first-order feature, is observed prior to the crystallization during cooling. The internal friction increases when the 'pre-solidification' effect occurs. The shear modulus increases until crystallization. An internal friction peak is attributed to the melting process observed during heating. The mechanism of the 'pre-solidification' transformation in Ga-In-Sn eutectic alloy is discussed.

Key words: Ga-In-Sn alloy, internal friction, liquid-liquid transition

Zjawiska przemian fazowych w eutektycznych stopach Ga-In-Sn, około temperatury pokojowej, badane są metodami analizy termicznej, tarcia wewnętrznego i XRD in-situ. Wyniki pokazują, że w dodatku do przemiany krzepnięcia, nowa przemiana tzw. „wstępne krzepnięcie”, o charakterze przemiany pierwszego rzędu, obserwowana jest przed krystalizacją podczas chłodzenia. Tarcie wewnętrzne zwiększa się, gdy występuje „wstępnie krzepnięcie”. Moduł sprężystości poprzecznej zwiększa się aż do krystalizacji. Wewnętrzny pik tarcia przypisany jest do topienia obserwowanego podczas ogrzewania. Omówiono mechanizm przemiany „wstępnego krzepnięcia” w eutektycznym stopie Ga-In-Sn.

1. Introduction

Ga-In-Sn eutectic alloys have attracted much attention due to the unique feature that exhibits typical metal properties in the liquid state even at room temperature. These alloys can be used as advanced flexible conductor [1], tip refrigerant [2] or mercury substitute [3], and attract potential users in electrical engineering, computer engineering, medicine, etc. Moreover, Ga-In-Sn alloys with the near-eutectic compositions have been used as a model material for the investigation of the crystallization process due to low melting temperature and a variety of phase diagrams of state [4]. Solidification and melting transformation of eutectic Ga-In-Sn alloys occur at around room temperature and bring in a few novel phenomena. It is crucial to understand these phase transformation behaviors of Ga-In-Sn eutectic alloy for practical applications.

In this paper, phase transformations in the Ga-In-Sn eutectic alloy are investigated by thermal analysis and internal friction around room temperature. Apart of the solidification

and melting transformation, a novel 'pre-solidification' effect is observed during cooling. The mechanism of the 'pre-solidification' effect is briefly discussed.

2. Materials and methods

The Ga-In-Sn eutectic alloy was prepared by melting in a furnace filled with pure argon. The raw materials for melting are high purity Gallium (99.99%), Indium (99.95%), and Tin (99.9%). The chemical composition of the Ga-In-Sn eutectic alloy is 69.0% Ga, 21.0% In and 10.0% Sn by weight. Thermal analysis of phase transformations was carried out in a differential scanning calorimeter (Diamond DSC, PerkinElmer). The cooling/heating rate was 5°C/min. The structural analysis of the Ga-In-Sn alloy during cooling was carried out by in-situ X-ray diffraction (XRD).

The internal friction and shear modulus were measured in a low-frequency subresonant internal friction spectrometer. The experimental set-up based on a conventional torsion

* INSTITUTE OF PHASE TRANSFORMATION AND COMPLEX MICROSTRUCTURE, SCHOOL OF MATERIALS SCIENCE AND ENGINEERING, SHANGHAI JIAO TONG UNIVERSITY, SHANGHAI 200240, CHINA

** ZHEJIANG LONGCAN INDUSTRIAL CO., LTD., HANGZHOU, CHINA

*** SCHOOL OF MEDIA AND DESIGN, SHANGHAI JIAO TONG UNIVERSITY, SHANGHAI 200240, CHINA

Corresponding author: ccding@sjtu.edu.cn

pendulum was modified as described in [5]. A vessel was used for holding a liquid sample whereas a bell-like cup was used as a sensor that should be immersed in the liquid sample and connected to an oscillating rod in the torsion pendulum. In order to avoid oxidation of liquid samples, the mechanical spectrometer was equipped with a vacuum pump and a gas shielding system (high purity argon). A computer controlled automatic system was designed to control experimental conditions and data processing. The mechanical loss, $\tan\phi$, (ϕ denotes the phase angle at which the strain lags behind an external stress applied on the specimen) of investigated melts was measured as a function of temperature with constant heating/cooling rate $1^\circ\text{C}/\text{min}$. Mechanical loss measurements were performed at constant driving frequency $f = 1.0$ Hz.

3. Results and discussion

Figure 1 shows the thermo-analytical curve of Ga-In-Sn alloy obtained during thermal cycle between -50°C and 50°C . Two exothermic peaks are observed at about -1.1°C and -35.2°C during cooling whereas only one endothermic peak occurs around 13.8°C during heating. The endothermic P3 peak observed during heating is associated with the melting transformation of the Ga-In-Sn alloy [6]. The exothermic P2 peak is believed to be induced by the crystallization nucleation process during solidification because the value of the released heat is close to the heat absorption during melting. The origin of the exothermic peak marked as P1 is unknown. It is clear, however, that a phase transformation occurred, which is identified in this work as the ‘pre-solidification’ and it would result in the change of physical properties, such as the viscosity and the coefficient of thermal expansion.

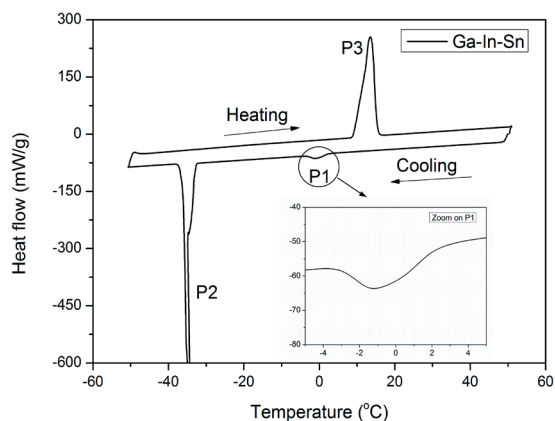


Fig. 1. DSC curve of Ga-In-Sn alloy during thermal cycle between -50°C and 50°C

An in-situ XRD analysis on the Ga-In-Sn alloy obtained during cooling from 50°C to -50°C is shown in Fig. 2. The results indicate that the Ga-In-Sn alloy exhibit liquid structure as cooled beyond -20°C . This indicates that the ‘pre-solidification’ transformation resembles a liquid-liquid transition. After being cooled to -40°C , the structure of the Ga-In-Sn alloy shows crystalline features. It is further

confirmed that the P2 exothermic peak during cooling in DSC analysis is caused by crystallization nucleation.

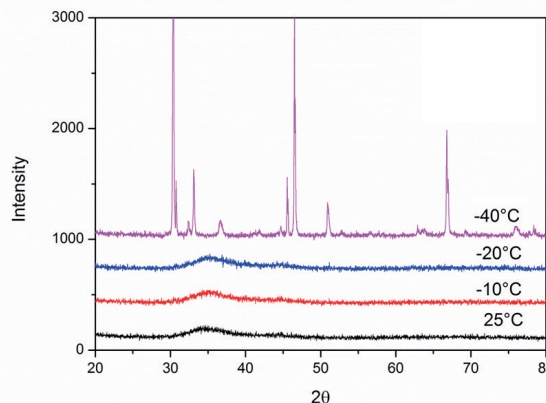


Fig. 2. In-situ XRD analysis on the Ga-In-Sn alloy during cooling from 50°C to -50°C

Figure 3 shows internal friction and shear modulus measured in the Ga-In-Sn alloy as a function of temperature during cooling. The internal friction increases at -0.2°C , while the modulus remains stable. This temperature is in good agreement with the occurrence of the P1 exothermic peak where the ‘pre-solidification’ effect is observed. As the temperature decreases to around -13.8°C , the internal friction decreases while shear modulus increases dramatically. A sudden rise of temperature of the Ga-In-Sn melts is also observed, which is caused by a huge heat release during crystallization. It can be concluded that the crystallization process occurs at -13.8°C during cooling in internal friction measurements, which is much higher as compared to the results obtained from thermal analysis. During heating, only one internal friction peak is observed around 21.5°C , which is accompanied by sharp decrease in the modulus (Fig. 4). This effect is caused by the melting of the Ga-In-Sn alloy. It is worth noting that the melting temperature of the Ga-In-Sn alloy in internal friction measurements is also higher than that in thermal analysis. It is concluded that the ‘pre-solidification’ behavior can lead to an increase in internal friction but does not affect the shear modulus of the Ga-In-Sn melts. By contrast, both the internal friction and shear modulus are sensitive to the melting and solidification processes.

Mechanical loss measurements and thermal analysis yield supplementary results suggesting that a first-order ‘pre-solidification’ transition can be observed between the melting and solidification temperatures. The structure of the Ga-In-Sn alloy after ‘pre-solidification’ indicates liquid features. Thus it is concluded that a first-order liquid-liquid transformation occurs in Ga-In-Sn super-cooled alloys. Liquid-liquid phase transitions have experimentally and theoretically been proved to occur in many one-component and multi-component systems [7-9]. Poole [10] proposed that the liquids having open molecular coordination environments at low pressure would show liquid-liquid phase transitions (also called liquid polymorphism) as the most promising candidates. In our case, the detailed mechanism of ‘pre-solidification’ behavior in the Ga-In-Sn alloys is not clear yet. But this metastable phase

transition can be clearly observed (and adjusted by alloying, which will be discussed in other paper) at suitable temperature without adding pressure. It was also not obscured by crystal nucleation in a considerable wide temperature range because the Ga-based alloys show huge undercooling. Hence, the Ga-In-Sn alloy is an ideal model material for excavating the intrinsic mechanism of the liquid-liquid transition.

Zu [11,12] investigated temperature-dependent discontinuous structural change in some binary liquids, such as In-Sn, Pb-Sn, Pb-Bi alloys by mechanical spectroscopy. The rise of internal friction peaks was observed as the liquid-liquid transition occurred. This effect was explained by the interface produced during transition [12]. It is important to emphasize that the shear modulus was not clearly changed during 'pre-solidification'. The internal friction peaks and associated mechanisms of dissipation of mechanical energy and variation the shear modulus in Ga-In-Sn alloys require further investigation.

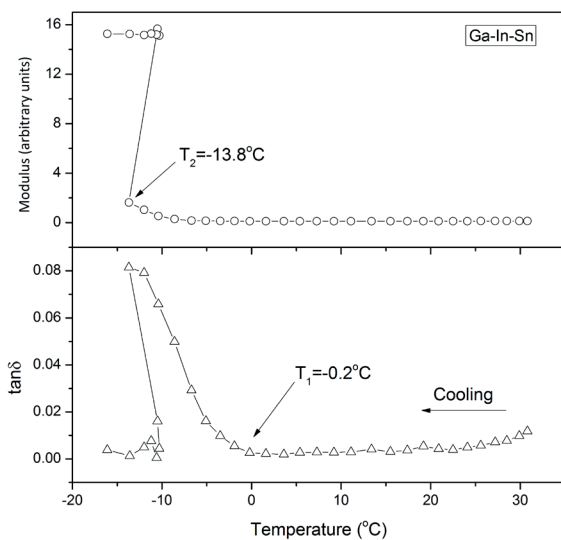


Fig. 3. Internal friction and shear modulus as a function of temperature during cooling of Ga-In-Sn alloy

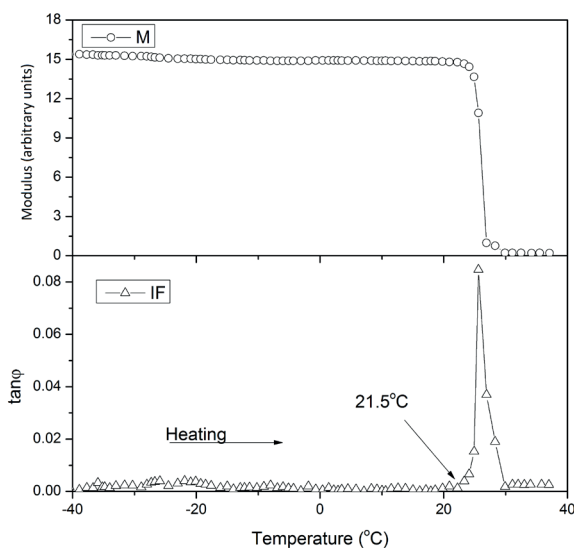


Fig. 4. Internal friction and shear modulus as a function of temperature during heating of Ga-In-Sn alloy

The solidification/melting transition temperatures determined from the internal friction measurements are much higher than temperatures deduced from the thermal analysis. It is tentatively explained that a sample is under time-independent static conditions during thermal analysis whereas it is subjected to an external harmonic perturbation stress field during mechanical loss measurements. The external torsional stress field might affect the solidification crystallization process which leads to higher crystallization temperature during cooling. This approach cannot explain, however, why the melting temperature rises during internal friction measurements during heating. One should also take into account that the sample in thermal analysis has a small volume with a ball shape. Under such circumstances, the surface tension plays an important role in the overall energy of the melts. These parameters affect the solidification/melting transition processes accompanied by huge volume change as well as the surface area change. Further experimental and theoretical research is required for the better understanding of the transition behavior in the Ga-In-Sn alloys.

4. Conclusions

The phase transformation of Ga-In-Sn alloys near room temperature was studied by thermal analysis, internal friction and in-situ XRD method. The experimental results showed that a first-order liquid-liquid transition, also called as the 'pre-solidification', can be experimentally observed prior to the solidification nucleation process during cooling of the Ga-In-Sn alloy. A melting phase transformation is observed only during heating. The internal friction is sensitive and powerful technique to reveal the 'pre-solidification' behavior while the variation in shear modulus can only reflect the melting and solidification process.

Acknowledgements

This work was supported by the National Youth Science Foundation (No. 51201100) and Zhejiang Longcan Industrial Co. Ltd., Hangzhou, China. We would like to thank Professor L.B. Magalas for valuable comments and suggestions.

REFERENCES

- [1] S. Zhu, J.H. So, R. Mays, S. Desai, W.R. Barnes, B. Pourdeyhimi, M.D. Dickey, Ultrastretchable fibers with metallic conductivity using a liquid metal alloy core, *Adv. Funct. Mater.* **23**, 2308-2314 (2013).
- [2] M. Hodes, R. Zhang, On the cooling potential of Galinstan-based minichannel heat sinks, 13th IEEE ITherm Conference, pp. 297-302 (2012).
- [3] P. Surmann, H. Zeyat, Voltammetric analysis using a self-renewable non-mercury electrode, *Anal. Bioanal. Chem.* **383**, 1009-1013 (2005).
- [4] S.V. Prokhorenko, Structure and viscosity of Gallium, Indium, and Tin in the vicinity of the crystallization temperature, *Materials Science* **41**, 271-274 (2005).

- [5] A.Q. Wu, L.J. Guo, C.S. Liu, E.G. Jia, Z.G. Zhu, Internal friction behavior of liquid Bi-Sn alloys, *Physica B* **369**, 51-55 (2005).
- [6] N.B. Morley, J. Burris, L.C. Cadwallader, M.D. Norbberg, GaInSn usage in the research laboratory, *Rev. Sci. Instrum.* **79**, 0561071-0561073 (2008).
- [7] Y. Katayama, T. Mizutani, W. Utsumi, M. Yamakata, K. Funakoshi, A first-order liquid-liquid phase transition in phosphorus, *Nature*, **403**, 170-173 (2000).
- [8] S. Aasland, P.F. McMillan, Density-driven liquid-liquid phase separation in the system $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$, *Nature* **369**, 633-636 (1994).
- [9] O. Mishima, Y. Suzuki, Propagation of the polyamorphic transition of ice and the liquid-liquid critical point, *Nature* **419**, 599-603 (2002).
- [10] P.H. Poole, T. Grande, C.A. Angell, P.F. McMillan, Polymorphic phase transitions in liquids and glasses, *Science* **275**, 322-323 (1997).
- [11] F.Q. Zu, Z.G. Zhu, L. J. Guo, X.B. Qin, H. Yang, W. J. Shan, Observation of an anomalous discontinuous liquid-structure change with temperature, *Physical Review Letter* **89**, 1255051-1255054 (2002).
- [12] F.Q. Zu, Z.G. Zhu, L.J. Guo, B. Zhang, J.P. Shui, C.S. Liu, Liquid-liquid phase transition in Pb-Sn melts, *Physical Review B* **64**, 1802031-1802034 (2001).

Received: 10 April 2015.