J Mater Sci (2009) 44:4856–4859
DOI 10.1007/s10853-009-3740-0

Generalized fragility of eutectic Al–Si alloys modified with phosphorus

Xigui Song · Xiufang Bian · Jingxiang Zhang · Jie Zhang · Xiangfa Liu

Received: 27 January 2009 / Accepted: 9 July 2009 / Published online: 24 July 2009

Abstract A new concept of fragility of superheated melt is used to analyze the viscosity of eutectic Al–12 wt%Si melts modified with phosphorus (P). The influence of P on the melt is investigated on the basis of Arrhenius law and fragility concept. The value of generalized fragility *M* named here is determined and available for evaluating the stability of modified eutectic Al–12 wt%Si melts and predicting the modifying effect of P.

Introduction

Viscosity is an important property of liquid metals and alloys. The viscosity results from the cohesion and molecular momentum exchange between fluid layers when they flow [1]. More and more research results suggest that liquid structures would have chemical short-range and medium-range order [1–4]. The behavior of liquid–liquid structural transition [5] manifested the occurrences of local clusters in liquid metals. Many experiments and computer simulations [6–11] showed that the properties of the liquid have a great effect on the mechanical properties and the quality of cast products.

A great deal of the efforts to study the modification of Al–Si alloys can date back to early 1920s under the demand of improving their mechanical products and industrial application [12, 13]. But less attention has been paid on the structures of Al–Si melts and their physical and chemical properties. In this paper, we test the viscosity of eutectic Al–Si melts modified with P and discuss the intrinsic mechanism of modification. The fragility theory proposed by Angell [14] is introduced to formulate the experimental results. The concept of fragility was originally served as a criterion to classify the glass-forming liquids [15]. Bian and his coworkers [16, 17] developed a new concept on the fragility of superheated melts based upon Angell's method. The new expression is given as

$$M_B = \left|\frac{\partial[\eta(T)/\eta(T_L)]}{\partial(T/T_L)}\right|_{T=T_L} = \left|\frac{\partial\eta_r}{\partial T_r}\right|_{T_r=1} \qquad (1)$$

where T_L is liquidus temperature, $\eta_r = \eta(T)/\eta(T_L)$, $T_r = T/T_L$. This definition is more convenient because the parameters (T_L, η_L) at liquidus temperature are easier to get than those (T_g, η_g) at glass transition temperature needed for Angell's fragility. Herein, the new fragility M_B is *generalized* and it can be used freely to analyze the modification of Al–Si alloys.

Experimental

The pure Aluminum (99.99 mass%) and ultra-high purity (99.9999 mass%) monocrystalline silicon were used for the fabrication of the Al–Si alloys. The high-purity Al–12 wt%Si alloy was made in a graphite crucible and melting in an electric resistance furnace. The phosphorus was added in the form of laminar Al–2.5%P (mass fraction) master alloy (Patent No. CN1317590A) at the mass percent level of 150, 200, and 300 ppm P, respectively. The melts were refined with C_2Cl_6 at 1023 K. Then the modified melt was poured into the cylindrical metal mold. The samples were machined to $\varphi27 \times 48$ mm^2 for viscosity measurements.

X. Song · X. Bian (✉) · J. Zhang · J. Zhang · X. Liu
The Key Laboratory of Liquid Structure and Heredity
of Materials, Ministry of Education, Shandong University,
Jinan 250061, China
e-mail: xfbian@sdu.edu.cn

X. Song
e-mail: sxglm@126.com

The thermodynamic properties of the eutectic Al–Si alloys were investigated by a Netzsch DSC404 calorimeter using pure indium (99.999 mass%) and zinc (99.999 mass%) standards. All differential scanning calorimetry (DSC) measurements were performed in a protection atmosphere flow (30 cm^3 min^{-1}) of nitrogen gas.

The viscosity was tested by an oscillating vessel viscometer (type: OSVM, made in Japan) for high-temperature melts. The samples were placed in a graphite vessel hung by a torsion suspension and sealed with a graphite cap, and the vessel was set in oscillation about a vertical axis, the oscillatory motion was gradually damped on account of frictional energy absorption and dissipation within the melt. The experiments were carried out under highly pure argon at a pressure of 1 atm as a shielding atmosphere to prevent the samples from oxidation. The samples were heated with the speed of 4 K/min to the highest measured temperature, holding temperature for 3 h. Finally, the viscosity was tested during the cooling process at the interval of 20–50 K. The value of the viscosity was collected by computer automatically for three or four times at each temperature, and the averaged values were used in this paper.

Results and discussion

The simplest viscosity–temperature relation, Arrhenius function, is suitable for molten alloys at temperatures at which viscosity is low (below 1 kPa s) [18]. The Arrhenius equation is expressed as

$$\eta = \eta_0 \exp\left(\frac{E_a}{RT}\right) \tag{2}$$

where η_0 is a pre-exponential constant for the viscosity at a high temperature T. Parameter R is the gas constant. E_a is the activation energy for viscous flow. So the fitting curves in Fig. 1 can be given based on Eq. 2. The related values are listed in Table 1.

Figure 1 shows the experimental values for viscosity η of the eutectic Al–12 wt%Si alloy and those modified with P. The addition of P evidently increases the viscosity of Al–12 wt% melts below 1050 K. The addition of phosphorus at a level of 150 ppm diminishes the viscosity of Al–12 wt%Si melt and it increases the viscosity as the additional level reaches to 200 and 300 ppm [19]. The more P concentrates, the larger the viscosity becomes. This puzzling influence on viscosity is probably in accordance with the complex solidification and eutectic growth of such eutectic Al–Si alloy [12, 13]. It can be seen from the fitting curves that the viscosity of modified Al–12 wt%Si melts increases more rapidly than that of unmodified melt with the decrease of the temperature. As mentioned above, P modification may result in the microstructural variation in the Al–12 wt%Si melts, and then changes the activation energy for viscous flow of these melts. We suggest that medium-range order or other contiguous order occur in modified eutectic Al–12 wt%Si melts because only short-range order exists in eutectic Al–Si melt which has been tested with high-temperature X-ray diffraction [1].

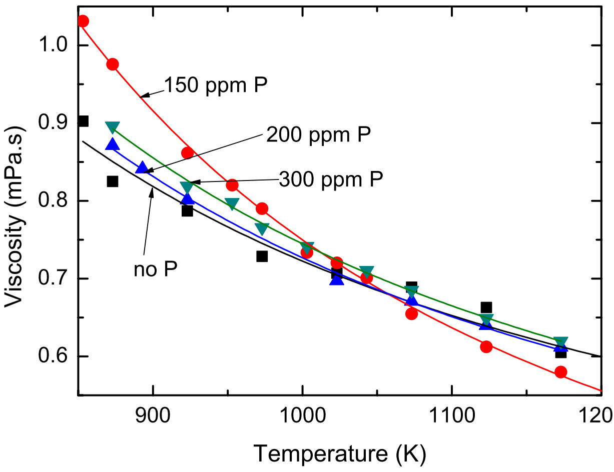

Fig. 1 Viscosity–temperature plot of Al–12 wt% Si melt and those modified with 150, 200, and 300 ppm P. The continuous curves are fitted based on Eq. 2. The discrete points are the measured viscosity values

DSC profile (Fig. 2) reveals that primary silicon begins to form when the additional level of phosphorus is more than 200 ppm. Interestingly, little phosphorus, 150 ppm P does not change the effect of the eutectic solidification. Research results [20] have shown that the purity of the eutectic alloys plays an important role in the eutectic nucleation. Ultra-high pure eutectic Al–Si alloys have refined microstructure without modification. If phosphorus concentration is less than 1 ppm, the alloy would freeze with a lamellar structure without any modifying agent. Higher addition of phosphorus causes the eutectic silicon to solidify in an acicular form [13]. The intricate influence of P may be the cause of the nonuniform variation of viscosity. The solidified microstructure variation could result from the viscosity changes [19].

Basically, the loss of kinetic energy would cause the ordering transformation of the molecules, which then crystallize at freezing point T_m, when a liquid is cooled. If the liquid is cooled at very quick quenched rate, crystallization can be avoided. The liquid structure therefore appears 'frozen' on the laboratory timescale [21–23]. The fragility m, which is defined as $m = \left|\frac{\partial \log \eta(T)}{\partial \left(T_g/T\right)}\right|_{T=T_g}$, is directly related to the slowing down of the dynamics. It is an index of how fast the viscosity increases while approaching the structural

Table 1 Characteristic values of Al–12 wt%Si melts modified with different levels of P

Additional levels of P (ppm)	η_0 (mPa s)	η_L (mPa s)	E_a (J mol^{-1})	T_L (K)	M	R^2
0	0.24	0.89	9316.50	843	1.33	0.97098
150	0.12	1.04	14942.99	847	2.12	0.99797
200	0.22	0.88	10062.28	861	1.41	0.99714
300	0.21	0.90	10362.10	865	1.44	0.99736

η_0, E_a are fitting parameters according to Eq. 2, T_L is the liquidus temperature obtained from Fig. 2 and η_L is the calculated viscosity at liquidus temperature according to Eq. 2. M is generalized fragility according to Eq. 5. R^2 is the adjusted square of correlation coefficient

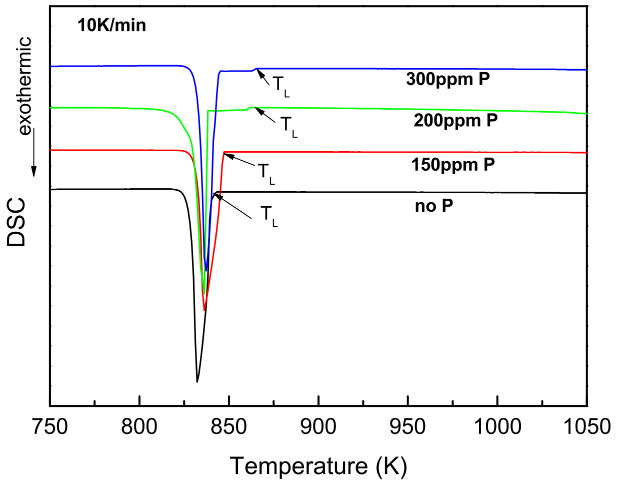

Fig. 2 DSC profiles of Al–12 wt%Si alloys with different levels of phosphorus. T_L is the liquidus temperature

arrest at glass transition T_g. Fragility m is an effective parameter to classify the glass forming ability (GFA) of liquid according to the its value, which is determined by the deviation of viscosity from the familiar Arrhenius law at supercooled temperature. The scaling temperature T_g is determined usually based on (a) T_g defined by scanning calorimetry at a standard rate and (b) the temperature at which certain relaxation times reach 100 s [24]. In fact, T_g is available only after glasses or supercooled liquids are obtained. Therefore, the question is attractive that whether there is another scaling temperature directly related to liquid melt or other expressions on fragility where T_g is not absolutely necessary. The generalized fragility M, scaled with liquidus temperature T_L, is introduced to evaluate the GFA of Al-based alloys and proven to be valuable [16].

Similar Angell plot [25] Fig. 3 can be obtained using the liquidus temperature T_L instead of T_g in Angell plot. The rapid variation of viscosity for superheated liquid is usually expressed as (M_A means according to Angell method)

$$M_A = \left|\frac{\partial \log \eta(T)}{\partial (T_L/T)}\right|_{T=T_L}. \tag{3}$$

Figure 4 shows the experimental viscosity scaled with η_L and the fitting curves according to Bian's plot method.

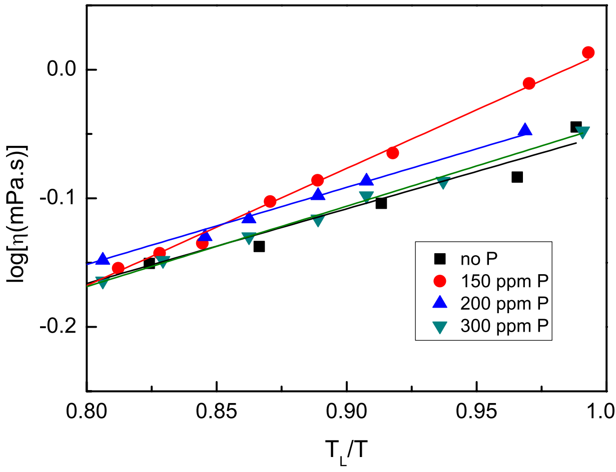

Fig. 3 Angell plot with T_L scaled temperature of experimental data (*discrete points*) and fitting curve (*solid line*) of Al–12 wt%Si melts with different levels of P

Figure 3 is of great importance to estimate changing rate of viscosity dependent on temperature. The viscosities of Al–12 wt%Si melts with little amount of P have no apparent differences at higher temperature about 913 K, but their increasing rate is apparently different with the decreasing temperature. By comparison, Fig. 4 clearly illustrates the dependence of activation energy E_a for viscous flow on the composition of the melts. The lower the curve, the larger is the E_a. Although phosphorus evidently increases E_a of Al–12 wt%Si melt, it is hard to find the quantitative relation between the increasing extent of viscosity and the P concentration.

The fragility can be calculated combining Eqs. 1 and 3 with Eq. 2, respectively.

$$M_A = \frac{E_a}{RT_L \ln 10} \tag{4}$$

$$M_B = \frac{E_a}{RT_L} \tag{5}$$

Actually, both expressions of fragility are identical except for the constant 1/ln 10 which comes from the common logarithm because they are decided by the same parameters T_L and E_a. For this reason, we use M_B, (named generalized

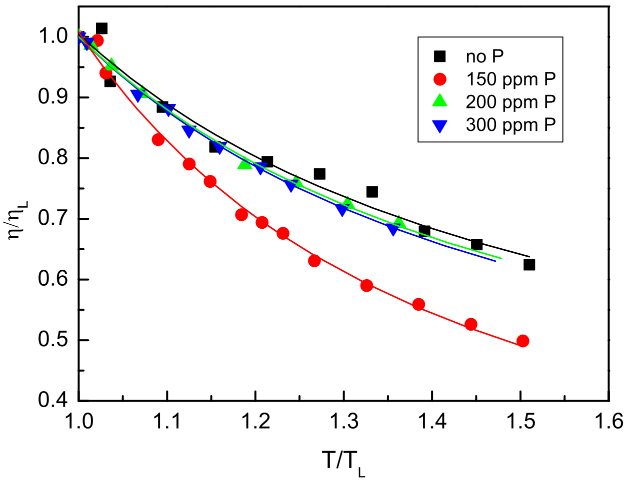

Fig. 4 Bian plot of reduced viscosity versus reduced temperature of Al–12 wt% Si melts with different levels of P

fragility *M* here), to determine the fragility of Al–12 wt%Si melts modified with P. From Table 1 and Fig. 1 we can see that Al–12 wt%Si melt with 150 ppm P has the largest *M* (>2) and its viscosity has acute changes. And the others have less *M* (<2). The critical value of *M* to predict the effect of modification of P could also be 2, which is similar to the evaluated GFA of alloys [16, 24]. Furthermore, it is well applied to evaluate the stability of a single alloy melt [26]. The liquid with a high value of *M* experiences rapid structure rearrangement toward the liquidus temperature. On the contrary, the liquid with low value of *M* holds more liquid structure when cooled down. So *M* can be used as a theoretical parameter reflecting the stability of liquid phase. The Al–12 wt%Si melt with 150 ppm P is the most unstable, on the contrary, the unmodified Al–12 wt%Si melt is most stable. This precisely indicates that only enough P concentration can modify the eutectic Al–12 wt%Si melt. The metastable melt with 150 ppm P is much more prone to modifying and producing primary silicon. Similarly, the melt present with primary silicon, which was modified with 200 or 300 ppm P, is relatively stable. Therefore, we suggest that if the generalized fragility *M* is more than 2, then the modification fails; if the generalized fragility *M* is between 1.33 and 2, then the modification succeeds. Generally, the term generalized fragility *M* is capable of predicting the modifying effect.

Conclusions

Our research indicated that P at 150 ppm level is not enough to modify eutectic Al–12 wt%Si alloy but it can dramatically increase activation energy E_a. Primary silicon is easily obtained when P concentration up to 200 ppm and viscosity rises with increasing P concentration.

The fragility with T_L-scaled temperature according to the Angell method is compared with that developed by Bian. It is found that both expressions of fragility are the same because they are decided by the same parameters T_L and E_a. The critical value of generalized fragility *M* is determined for Al–12 wt%Si melt with different levels of P, and it is capable of predicting the modifying effect of phosphorus.

Acknowledgements We would like to acknowledge financial support from the National Basic Research Program of China (973 Program 2007CB613901), the National Nature Science Foundation of China (Grant Nos. 50631010 and 50471052) and the Natural Science Foundation of Shandong province (Grant No. Z2008F08). We also acknowledge the support from Shandong Distinguished Youth Scholar Fund (J200817).

References

1. Bian XF, Zhang JX, Jia YB (2005) Chin Phys Lett 22:644
2. Gruner S, Hoyer W (2008) J Alloys Compd 460:496
3. Zhang L, Wu YS, Bian XF, Li H, Wang WM, Wu S (2000) J Non-Cryst Solids 262:169
4. Bian XF, Pan XM, Qin XB, Jiang MH (2002) Sci China 45:113
5. Wang YQ, Wu YQ, Bian XF (2007) Chin Phys Lett 24:2028
6. Bian XF, Liu XF, Ma JJ (1999) Heredity of metals. Shandong Science and Technology Press, Jinan
7. Liu XF, Bian XF, Qi XG, Ma JJ (1997) JOM 11:40
8. Li H, Pederiva F (2003) Phys Rev B 68:054210
9. Li H (2004) J Phys Chem B 108:5438
10. Schastlivtsev VM, Tabatchikova TI, Yakovleva IL (1995) Phys Met Metallogr 80:668
11. Kataev VA, Letov MV, Starodubtsev YuN, Tsepelev VS, Kuzevanova LA (2001) Phys Met Metallogr 92:123
12. Shankar S, Riddle YW, Makhlouf MM (2004) Metall Mater Trans A 35:3038
13. Hegde S, Prabhu KN (2008) J Mater Sci 43:3009. doi:10.1007/s10853-008-2505-5
14. Angell CA (1985) J Non-Cryst Solids 73:1
15. Hutchinson JM (1998) Polym Int 47:56
16. Bian XF, Sun BA, Hu LN (2005) Phys Lett A 335:61
17. Si PC, Bian XF, Zhang JY, Li H, Sun MH, Zhao Y (2003) J Phys Condens Matter 15:5409
18. Hrma P (2008) J Non-Cryst Solids 354:3389
19. Song XG, Bian XF, Zhang JX, Zhang J (2009) J Alloys Compd 479:670
20. McDonald SD, Nogita K, Dahle AK (2004) Acta Mater 52:4273
21. Debenedetti PG, Stillinger FH (2001) Nature 410:259
22. Scopigno T, Ruocco G, Sette F, Manaco G (2003) Science 302:849
23. Angell CA (1995) Science 267:1924
24. Zhao Y, Bian XF, Hou XX (2006) Physica A 367:42
25. Martinez LM, Angell CA (2001) Nature 410:663
26. Sun BA, Bian XF, Hu J, Mao T, Zhang Y (2008) Mater Charact 59:820