The Rate of Coarsening of the Microstructure in Semi-Solid Aluminium Alloys

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Abstract : In semi-solid metal processing, the temperature is between the solidus and the liquidus. To behave thixotropically, the microstructure must be non-dendritic and consist of spheroids of solid in a liquid matrix. Recrystallisation and Partial melting (RAP) and the cooling slope (CS) are two potential routes to suitable non-dendritic starting material. Here the rate of microstructural coarsening of such materials in the semi-solid state is compared with rates found in the literature.

The rate of coarsening depends on the liquid fraction but RAP route 2014 alloy with 37% liquid coarsens slightly more *slowly* than the CS route 2014 alloy with a lower liquid fraction of 17%, contrary to expectations. For the CS route, an increase in liquid fraction resulted in faster coarsening. A modified 2014 alloy with the Fe, Mn and Zn stripped out of the composition gave a relatively high coarsening rate. The coarsening rate was also relatively high for CS 201 alloy in comparison with either RAP 2014 or CS 2014. Low coarsening rates are thought to be associated with the presence of particles which are inhibiting the migration of liquid film grain boundaries. This could be the result of pinning or of the liquid film impeding diffusion at the boundary.

Keywords: coarsening; semi-solid; 2014 alloy; recrystallisation and partial melting; cooling slope.

1 Introduction

Semi-solid processing takes place between the liquidus and solidus temperatures and requires the microstructure in the semi-solid state to consist of spheroids of solid in a liquid matrix [1]. The material then behaves *thixotropically* i.e. it flows when sheared but thickens when allowed to stand. Hence, processing routes based on this behaviour are termed *thixocasting* (when the liquid fraction is relatively high) and *thixoforging* (when the liquid fraction is relatively low). The term thixoforming is either used to denote a process intermediate between these two in terms of liquid fraction or as a general description for the semi-solid processing routes which involve reheating solid into the semi-solid state. During reheating, the microstructure evolves; extensive coarsening will have a deleterious effect on the final mechanical properties of the

thixoformed component. As a rule, if the spheroid size on forming is greater than about 100 μms the properties are likely to be unacceptable. In addition, if the spheroid size is too large it will limit flow into thin sections of the die (with a 1 mm thickness section equivalent to 10 spheroid diameters if each spheroid is 100 μms).

This paper compares the rates of coarsening in material produced by two different routes: recrystallisation and partial melting (RAP) [2] and cooling slope casting (CS) [3]. RAP is used for the commercial production of aluminium alloy components. CS is associated with the new rheocasting route (NRC) [4,5] and also has wider potential applications [e.g. 6,7] although there is the potential for incorporation of oxide. RAP involves material which has been previously worked, e.g. by extrusion or rolling. When this material is reheated into the semi-solid state it recrystallises and the first liquid to form tends to be on the recrystallised boundaries. RAP is distinct from SIMA (strain induced

melt activated) [8] in that the working is ‘warm’ whereas in SIMA it is ‘hot’. Many aerospace alloys are supplied in the worked state and therefore are immediately suitable for reheating and thixoforming. In addition, the spheroids tend to be very well rounded in comparison with those produced by liquid state routes such as magnetohydrodynamic (MHD) stirring, tending to flow better [9].

In the cooling slope route, liquid metal is poured onto a chilled slope and as it runs down, solid nuclei develop. These tumble over each other in the flow, preventing dendrite development and hence producing a solid material which is suitable for reheating for thixoforming [10].

Classically, for low fractions of solid f_s , the LSW theory applies [11-13]:

$$\bar{d}^3 - \bar{d}_0^3 = Kt \quad (1)$$

where $\bar{d}$ is the average particle diameter at time t , $\bar{d}_0$ is the average particle diameter at time $t = 0$ and K is the coarsening rate constant. For higher f_s , Annavarapu and Doherty [14] proposed the liquid film migration model where the coarsening rate should increase as the f_s increases. However, experimental results [15] show the opposite. A modified liquid film migration model was therefore developed by Manson-Whitton et al. [15] to take into account the necks between the contacting solid particles. The transition between the two occurs at $f_s \sim 0.7$. Other workers [16,17] have observed that at high f_s the coarsening is controlled by diffusion through the liquid rather than by solid-solid contacts. Manson-Whitton et al. [15] and de Freitas et al. [18] have discussed the inhibition of coarsening by particles present in grain boundary liquid films.

In this paper, aluminium alloy material produced by this route and by RAP is analysed and compared with results in the literature. A longer, more detailed version has previously been presented [19]. The materials are RAP 2014 (a conventionally wrought alloy); CS 2014; a modified 2014 without the minor elements Fe, Mn and Zn and with relatively low Si produced by CS; and alloy 201 (a high strength casting alloy) produced by CS. The alloys have previously been thixoformed and the results presented [20,21].

2 Experimental

The condition of starting materials is summarized in Table 1. The extruded 2014 was used for both the RAP route and for remelting for the CS. The details for the cooling slope route are given in [19]. The modified 2014 and the 201 were both treated with the CS. A salt bath furnace was used to study the microstructural evolution

in the semi-solid state. The temperatures were originally chosen to give fractions of liquid suitable, or approaching those suitable for, thixoforming of the alloys concerned. It is therefore not the case that the same liquid fraction has been used for each alloy. The samples were 8 mm x 8 mm x 15 mm and were monitored with a thermocouple in a hole in the centre of the specimen. The isothermal holding temperatures are shown in Table 2 along with the liquid fraction determined with differential scanning calorimetry (DSC). After heat treatment, the samples were ground, polished and examined optically. Image analysis was used to obtain the grain/rosette size ($\bar{d} = (4A/\pi)^{1/2}$, where A is area of rosette) and the coarsening rate constants calculated using equation (1). The term ‘rosette’ is used here to describe the microstructural features which are not dendrites but are not fully rounded spheroids either.

Micrograph sequences for isothermal holding in the semi-solid state have been previously presented for extruded 2014 (T6 condition), cooling slope modified 2014 and cooling slope 201 [20]. The results for cooling slope 2014 are shown in [19]. We focus here on results for the coarsening constants.

3 Results and Discussion

Fig. 1 shows the results for the evolution of the cube of the average globule diameter as a function of the isothermal soaking time in the semi-solid state for the various alloys in Table 1. The intercept is the value of $\bar{d}_0^3$. As commented previously, the amounts of liquid are not directly comparable. However, it is clear that the alloy 2014, made by either the CS or the RAP route gave slower coarsening kinetics. The values of the coarsening rate constant are shown on the graph. A lower coarsening rate constant was observed for the RAP route than for the CS route and a lower coarsening rate for the CS route at lower heating temperature with lower fraction liquid. Compared with alloy 2014, relatively faster coarsening rate kinetics were shown by modified alloy 2014 and alloy 201 made by CS.

Coarsening rate thus appears to be related to the initial microstructure, i.e. RAP or CS, and to the alloy composition. For example, for a similar initial microstructure from cooling slope casting, a higher coarsening rate constant was obtained for modified 2014 and alloy 201 than for unmodified 2014.

Some liquid pockets are present within the primary phase. An example is shown in Fig. 2.

Table 1. Starting Materials with Wrought and Cast Handbook Values Shown in Bold for Comparison (adapted from [19])

Alloy	Cu	Mg	Si	Fe	Mn	Zn	Cr	Ti	Ag	Bal. Al	As-Received Condition
201	4.35	0.36	<0.05	<0.02	0.34	<0.02	<0.01	<0.01	0.60		Direct Chill cast, 97 mm diameter
201	4.0-5.2	0.15-0.55	<0.10	<0.15	0.2-0.5	-	-	0.15-0.35	0.4-1.0		
2014	3.91	0.47	0.83	0.29	0.55	0.06	0.01	0.07			Extruded and T6 heat treated in 50 mm diameter
Mod2014	3.87	0.6	0.14	<0.01	<0.01	<0.001	-	-			Direct Chill cast, 73 mm diameter
2014	3.9-5.0	0.2-0.8	0.5-1.2	<0.7	0.4-1.2	<0.25	<0.1	<0.15			

All compositions are in wt.%. For experimental materials, the compositions were measured using the Inductively Coupled Plasma Emission Spectroscopy (ICPES) method. ‘Mod’ refers to ‘Modified’ Alloys.

Table 2 Temperatures of Isothermal Holding and Corresponding Liquid Fractions (adapted from [19])

Alloy	Isothermal Holding Temperature (°C)	Liquid Fraction (%) (Error $\pm 3\%$)
Extruded 2014 in T6 heat treatment condition	625	37
Extruded 2014 in T6 condition and then cooling slope treated (assuming identical DSC behaviour to the material above)	620	28
	610	18
Modified 2014 cooling slope treated	631	45
Alloy 201 cooling slope treated	620	20

During partial melting and then holding in the semi-solid state, coarsening first proceeds through the coalescence of dendrite arms (Fig. 2). After coalescence, phase coarsening will take place through the dissolution of the small globules and the grain numbers will then decrease [22]. In the alloys examined here, micrographs show coalescence is having a relatively minor effect after the very initial stages. CS 2014, CS cast modified 2014 and alloy 201 all have similar Cu contents. The differences in coarsening rates are thought to be due to secondary phases [15-18]. The precipitation hardening particles are not responsible because they tend to dissolve below the solidus. It is more likely to be the Fe, Mn-based intermetallic particles, which are insoluble, which are giving the pinning effect. Hence, the

modified alloy, with these elements stripped out coarsens fast. This could be the result of pinning or of the liquid film impeding diffusion at the boundary. It is likely that the difference between RAP 2014 and CS 2014 is due to differences between quantities and distributions of the intermetallic particles.

Figs. 3 and 4 summarise data from the literature. The majority of the results in Fig. 4 are for wrought alloys which are likely to have minority phase particles present. The exceptions are circled. The AlCu4.5Mg1.5 [14] results are for a grain refined alloy and it may be the Ti-rich grain refining particles which are inhibiting grain boundary migration in the semi-solid state. There are also some results [24] which may be explained by the presence of porosity in small sprayforming batches [31].

Fig. 1 Evolution of the average globule diameter d as a function of isothermal soaking time at 610 to 631°C in the semi-solid state for different materials (adapted from [19]). Dotted lines represent evolution according to $d^3 = d_0^3 + Kt$. The unit for the coarsening constant K in each case is $\mu\text{m}^3\text{s}^{-1}$. R^2 is the regression coefficient. Note that, more formally, the errors are such that the coarsening rate figures cannot be quoted to this precision, and should be rounded to 170, 190, 260, 1400 and 2200 $\mu\text{m}^3\text{s}^{-1}$.

Fig. 2 Presence of entrapped liquid in primary grains in cooling slope modified alloy 2014 soaked for 5 min at 631°C (adapted from [19]). In grain A, a large liquid droplet (indicated by arrow B) is apparently about to detach itself from the grain boundary and another one (arrow C) is going to form from the liquid on the grain boundary.

Fig. 3 Coarsening coefficient (K) vs. temperature assuming $d^3-d_0^3=Kt$ for Al alloys showing generally high K ($>600\mu\text{m}^3/\text{s}$) in casting Al alloys and generally low K ($<600\mu\text{m}^3/\text{s}$) in alloys which would normally be wrought (adapted from [19]). A magnified view for the $0-650 \times 10^{-18} \text{m}^3/\text{s}$ range is shown in Fig. 4.

Fig. 4 Magnified view of the $0\text{--}650 \times 10^{-18} \text{ m}^3/\text{s}$ range in K in Fig. 3 (adapted from [19]). The majority of the results here are for alloys which are normally wrought. A few casting alloys give results in this range and these are circled. These are: grain refined DC-cast AlCu4.5Mg1.5 [14]; chill-cast Al-6.7Cu [14]; spray formed Al-4Cu [23]; SIMA Al-4Cu with grain refiner [28]; and SIMA AlSi7Mg0.6 [22] (all compositions in wt%).

4 Conclusions

Two potential routes to suitable material for thixoforming are RAP and CS. Here the microstructural coarsening of such materials in the semi-solid state has been analysed. A lower coarsening rate was observed for RAP route 2014 than for CS route 2014 despite the higher fraction liquid for the former. For the CS route, an increase in fraction liquid gave a higher coarsening rate. A relatively high rate was observed for ‘modified’ 2014 with the Fe, Mn and Zn not present in the composition and also for CS 201. Dendrite arm coalescence is only contributing to coarsening in the very initial stages with CS material. The lower coarsening rate in CS 2014 in comparison with other alloys is thought to be due to

the presence of secondary phases in the 2014, which are pinning the liquid boundary migration. The particles must be resistant to dissolution and are likely to be insoluble Fe, Mn-based intermetallics. Analysis of data from the literature

suggests that those alloys which give relatively low coarsening coefficients generally have pinned liquid film boundaries (e.g. due to intermetallics, porosity, or grain refining species such as Ti). Thus, wrought alloy compositions tend to coarsen more slowly than cast, as do alloys which contain grain refiner.

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References

- [1] FLEMINGS M C. [J]. Metall. Trans. A, 1991, A22, 957.
- [2] KIRKWOOD D H, SELLARS C M, ELIAS BOYED L G. [P] 'Thixotropic Materials' European Patent No. 0305375 B1, 28 October 1992.
- [3] HAGA T, KOUHA H, MOTOYAMA N, INOUE N, SUZUKI S. [C]// Proceedings of ICAA7, Aluminium Alloys: Their Physical and Mechanical Properties, Charlottesville, VA., Part 1 (1998) 327-32, Publ. Trans Tech Publications 2000.
- [4] KANEUCHI T, SHIBATA R, OZAWA M. [C]// Proc. 7th Int. Conf. on Advanced Semi-Solid Processing of Alloys and Composites, Tsukuba, Japan, 2002, edited by Y. Tsutsui, M. Kiuchi, K. Ichikawa (National Institute of Advanced Science and Technology and the Japan Society for Technology of Plasticity 2002) p.145.
- [5] MITSURU A, HIROTO S, YASUNORI H, TATSUO S, SATORU S, ATSUSHI Y. [P] Method and Apparatus for Shaping Semisolid metals, UBE Industries Limited, Patent EP 0745694 A1 (1996).
- [6] HAGA T. [J]. J. Mater. Process. Technol., 2002, 130-1: 558.
- [7] LIMA FILHO A D, YAMASAKI M I. [J]. Solid State Phenomena, 2006,116-117: 433.
- [8] YOUNG K P, KYONKA C P, COURTOIS J A. [P] "Fine Grained metal composition", US Patent No. 4,415,374, 30 March 1982.
- [9] LIU T Y, ATKINSON H V, KAPRANOS P, KIRKWOOD D H, HOGG S C. [J] Metall. Mater. Trans. A, 2003, 34: 1545-1554.
- [10] CARDOSA LEGORETTA E, ATKINSON H V, JONES H. [J]. J. Mater. Sci., 2008, 43: 5456-69.
- [11] GREENWOOD G W. [J]. Acta Metall., 1956, 4: 253.
- [12] LIFSHITZ I M, SLYOZOV V V. [J]. J. Phys. Chem. Solids, 1961, 19: 35.
- [13] WAGNER C. [J]. Z. Electrochemie, 1961, 65: 581.
- [14] ANNAVARAPU S, DOHERTY R D. [J]. Acta Metall. Mater., 1995, 43: 3207-3230.
- [15] MANSON-WHITTON D, STONE I C, JONES J R, GRANT P S, CANTOR B. [J]. Acta Mater., 2002, 50: 2517-2535.
- [16] KIM S S, YOON D N. [J]. Acta Metall., 1983, 31: 1151.
- [17] BOETTINGER W J, VOORHEES P W, DOBBYN R C, BURDETTE H E. [J] Metall. Trans.A, 1987, 18A: 487.
- [18] DE FREITAS E R, FERRACINI Jnr. E, FERRANTE M. [J]. J. Mater. Process. Technol., 2004, 146: 241.
- [19] ATKINSON H V, LIU Dan. [J]. Mater. Sci. Engng. A, 2008, 496: 439-446.
- [20] LIU Dan, ATKINSON H V, KAPRANOS P, JIRATTITICHAROEAN W, JONES H. [J]. Mater. Sci. Engng. A, 2003, A361: 213-224.
- [21] LIU Dan. Thixoforming of High Performance Alloys Mainly Based on the Al-Cu System [PhD thesis]. University of Sheffield, 2003.
- [22] LOUE W R, Suery M. [J]. Mater. Sci. Engng. A, 1995, A203: 1-13.
- [23] GRANT P S, UNDERHILL R P, KIM W T, MINGARD K P, CANTOR B. [C]. Spray Forming 2 (edited by John V. Wood), p. 45. Woodhead, Cambridge, England (1993).
- [24] KIM Hee-Soo. [PhD thesis]. Univ. of Oxford, UK, 2003
- [25] PITTS H. [PhD Thesis]. Semi-solid Processing of Aluminium 6061, University of Sheffield, 1999, p.52
- [26] CHAYONG S. [PhD Thesis]. Thixoforming Processing of Aluminium 7075 Alloy, Univ. of Sheffield, 2002, p.98
- [27] SALVO L, SUERY M, CHARENTENAY Y De, LOUE W. [C]. Proc. 4th Int. Conf. Semi-Solid Processing of Alloys and Composites, Sheffield, UK, June 19-21, 1996, 10-15.
- [28] FERRANTE M, FREITAS E de. [J]. Mater. Sci. Engng. A, 1999, A271: 172-180
- [29] KIUCHI M, YANAGIMOTO J, SUGIYAMA S. [C]. Proc. 5th Int. Conf. on Semi-Solid Processing of Alloys and Composites, Colorado, USA, June 23-25, 1998, 589-96.
- [30] ZOQUI E J, SHEHATA M T, PAES M, KAO V, ES-SADIQI E. [J]. Mater. Sci. Eng.A., 2002, A325:38-53.

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- [31] GRANT P S. Oxford University, Private Communication,
Jan 2008.