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Role of ambient oxygen in the stabilisation of single aluminium alloy films

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Abstract

Aluminium-based single films were pulled out of a melt using circular wire frames and characterised with respect to their stability under varied conditions. Pure Al, AlSi9 and AlSi9Mg0.6 alloys as well as particle reinforced composites based on the same alloys but adding different amounts of stabilising SiC or TiB₂ particles were prepared. The velocity at which films were drawn was varied to investigate their solidification as well as their oxidation behaviour. In order to study the influence of the oxygen content of the foaming atmosphere a chamber was manufactured that allows for pulling single films under defined conditions. It was found that films without Mg were less stable than Mg-containing ones and even the addition of particles to such Mg-free alloys results in no improvement. In contrast, films made of AlSi9Mg0.6 were more stable and required only a small amount of oxygen (> 200 ppm O₂), but in general some oxygen has always to be present to obtain a stable film. It was found that the more particles are contained in the composite and the slower the film gets pulled, the lower the required oxygen content is.

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1. Introduction

Metal foams can be manufactured in different processes depending in which state of matter the metal is processed (Banhart (2001), Wübben and Odenbach (2005)). Especially the liquid metal route is an attractive way from the economical point of view and covers a large range of different materials and compositions. However, it is still not fully understood how the foam is stabilised (Banhart (2006), and Haibel et al. (2006)). Metallic foams are

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usually studied after solidification, whereby a detailed investigation of the oxygen layer as well as the arrangement of solid stabilising particles is possible (Dudka et al. (2008), Kadoi and Nakae (2011)).

Studies of metallic foams using different types of blowing gases have already been done (Babcsán et al. (2004), and Leitmeier et al. (2002)). Our interest is captured by the oxidation of solid-gas interfaces. Our basic motivation is to learn about the complex foam stabilisation mechanism by studying a simpler system, namely the model system of single films and to identify the role of particles as well as of oxygen for foam stabilisation.

2. Experimental Procedure

2.1. Sample preparation

Three particle-free alloys were prepared to investigate alloys without the effect of particle stabilisation: commercially pure Al, an AlSi9 alloy and AlSi9Mg0.6 modified by adding 0.6 wt.% Mg to the AlSi9 alloy by using an electrical resistance furnace in an open atmosphere, followed by stirring and casting. In addition, two SiC-containing as well as three TiB₂-reinforced composites were prepared. The former commercial composite contained 20 vol.% SiC particles ('p') with a mean particle size of 10 µm. The trade name of this material is F3S20S, producer Alcan, Montréal, Canada. We further used the particle-free AlSi9Mg0.6 alloy for diluting the previously mentioned F3S20S to the second desired concentration of 10 vol.% SiC particles.

To study the effect of the alloying elements in combination with reinforcing particles, we prepared pure Al, AlSi9 and an AlSi9Mg0.6 alloy each containing 6 vol.% TiB₂, via a flux-assisted in-situ synthesis route (Kumar et al. (2007)). The mean particle size of TiB₂ is smaller in comparison to SiC and lies between 1–3 µm. For preparing the precursor, the composites were molten in an alumina crucible at 750 °C and cast into an open graphite mold. Each precursor material was prepared by cutting the ingots to pieces of 80 g. The composites used are summarised and listed in table 1.

Table 1: Composites prepared for film pulling

Matrix composition	Particle type	Particle content, vol. %	Required oxygen content in ppm			
			Without stirring		With stirring	
			1 mm/s	10 mm/s	1 mm/s	10 mm/s
Al			Ambient atmosphere, 21x10 ⁴ (8 mm in O)			
AlSi9			Not stable at all			
AlSi9Mg0.6		1200	1200	1000	1500	
Al	TiB ₂	6	Ambient atmosphere, 21x10 ⁴ (8 mm in O)			
AlSi9	TiB ₂	6	Not stable at all			
AlSi9Mg0.6	TiB ₂	6	-	-	300	500
AlSi9Mg0.6	SiC	10	2500	1000	500	1500
AlSi9Mg0.6	SiC	20	5000	500	200	400

2.2. Film pulling process

Our aim was to study the effect of four different parameters on film stability: the oxygen content of the surrounding atmosphere, the drawing velocity, the alloy composition as well as the type and content of solid particles. We manufactured a vacuum chamber to control the surrounding oxygen content from 10⁻⁸ ppm to 21 % O₂ by establishing a constant flow of a defined mixture of Ar and air, see figure 1. The oxygen level was analysed via an "Oxygen Service Controller II" from Prozess-Informatik GmbH, Germany. In the centre of this controlled chamber a small furnace was mounted to re-melt the precursor at the desired temperature of 680 °C. The drawing velocity was varied from 1 to 10 mm/s to study the influence of time till solidification or the effect of drainage. The adjustment was undertaken by a manipulator which was actuated by a stepper motor controlled via the software "CME2". A chopper disk-belt system was set up on top of the film pulling chamber. Films solidified within 5 s or 10 s for 10 mm/s or 1 mm/s pulling velocity, respectively. Circular wire frames (∅ = 12 mm) were used to pull films out of a crucible filled with the liquid material. The corresponding temperature profiles are displayed in figure 2.

Well-defined film pulling conditions require the elimination of the oxide layer occurring on top of the melt to obtain a fresh, almost uncontaminated surface. Oxide films usually start as simple amorphous (non-crystalline)

layers such as Al₂O₃ or MgO, which quickly convert to crystalline products as they grow [33]. Even at the lowest oxygen level of 10⁻⁸ ppm it is impossible to avoid surface oxidation completely.

We mounted a simple steel grid directly above the circular wire frame to remove or at least to destroy the oxide layer immediately before the film gets pulled. Furthermore, as particles are able to settle rapidly inside a molten alloy and thus the nominal particle content of the composite might not be guaranteed inside a film (Kumar et al. (2010)), we fixed a stirrer inside the chamber to achieve a homogenous distribution directly before pulling. Stirring was achieved by a DC motor, the rotating velocity of which was adjusted manually. Due to these modifications we can guarantee the selected fraction of particles in a film as well as avoid coarse surface oxides.

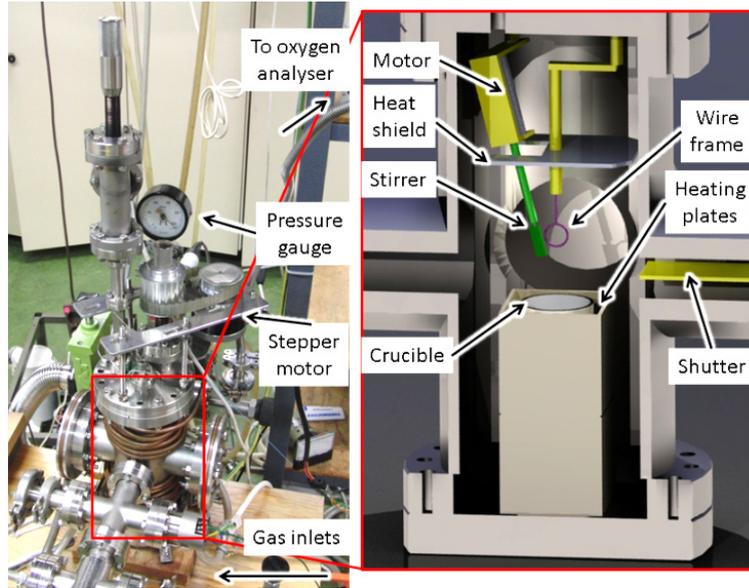


Figure 1: Film pulling apparatus with automated adjustment for 1–10 mm/s pulling velocity, with stirring device; left: photograph of the chamber; right: cross section of the chamber.

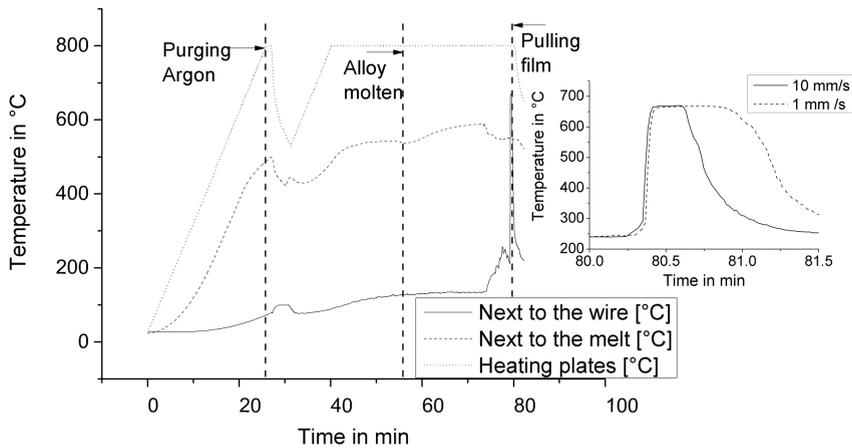


Figure 2: Temperature profile of film pulling process; Inset shows the moment of film pulling and solidification for 1 and 10 mm/s (next to the wire).

2.3. Evaluation of film stability

Films were examined by taking pictures against an illuminated background after solidification and then binarising and analysing them with the software “ImageJ”. The fraction of stabilised film, represented by the black areas in figure 3 is called the film area A . Percentages were calculated using:

$$A = \frac{A_S}{A_0} \times 100\%, \quad (1)$$

with the stabilised film area A_S and the wire frame area A_0 . Small cracks on the stabilised film areas are caused by solidification shrinkage. Films were further investigated by metallographic analysis to obtain film thicknesses and to characterise the arrangement of solid particles.

3. Results

Pure Al, AlSi9 as well as their TiB₂-reinforced composites were not stable even at 21 % O₂ and 12 mm wire frame diameter, whereupon no further investigation in an oxygen-reduced atmosphere was performed. For pure Al and Al + 6 vol.% TiB₂ the frame diameter had to be reduced to 8 mm at 21 % oxygen to obtain a stable film. AlSi9 and its particle-reinforced counterparts were again not stable at all. Thus we concentrated our further study on the basic particle-free alloy of AlSi9Mg0.6 and its composites containing SiC and TiB₂ particles.

During this first experimental series the relation between the ambient oxygen content and a varying amount of SiC particles was investigated. In figure 3, the increasing film sizes for SiC composites against the increasing oxide content can be seen. For film sizes > 85 % (points of interest, figure 3) films became stable. A threshold value of 85 % was determined considering the area reduction due to crack formation during solidification, although the film was still stable. Stirring directly before pulling is essential to obtain defined starting conditions and to avoid irreproducible and confusing results. The oxygen content required for TiB₂-reinforced AlSi9Mg0.6 alloy was 500 ppm or 300 ppm for 10 mm/s and 1 mm/s pulling velocity, respectively. All results are given in table 1.

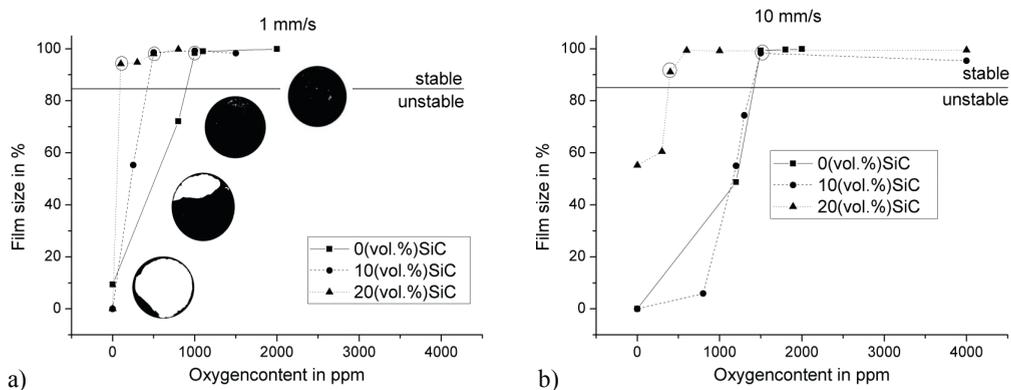


Figure 3: Film size vs. oxygen content; a) 1 mm/s b) 10 mm/s, points of interest marked by a circle; binarised images of film evolution are exemplarily shown for the particle-free alloy pulled at 1 mm/s.

4. Discussion

The interplay of forces which might stabilise single films is discussed by separation into four different aspects, which are the alloying elements, the particle fraction, the applied pulling velocity as well as the oxygen content. Starting with the variation of alloying elements from pure Al over AlSi9 to AlSi9Mg0.6 alloys, it was obvious from the very beginning that films of Mg-free alloys are less (pure Al) or even not stable at all (AlSi9). An addition of solid particles to pure Al and AlSi9 does not support film stability. One reason might be the fact that Mg is able to

build MgO, which enhances the viscosity of the Al alloy used (Kim et al. (2006)). However, during our experiments films solidify within 5 s to 10 s and thus viscosity will not play a big role. But the high affinity of Mg to oxygen and the increased oxidation rate at the solid-gas surface, which is generated by adding only 1 wt.% Mg to an Al alloy as demonstrated by Campbell, might be one reason for the high stability of Mg-containing alloys (Campbell (1991), and Belitskus (1971)). This suggests a closer look at the oxidation behaviour and its role as a stabilising mechanism especially for AlSi9Mg0.6 and its composites.

The experimental series of pulling films at a defined oxygen atmosphere yields the most important finding: no film can be pulled in an inert atmosphere (< 200 ppm O₂) even at the maximum SiC or TiB₂ content, lowest pulling velocity and minimum frame size. The film size first increases with increasing oxygen content of the surrounding atmosphere until a threshold value is reached and the entire film is stable. Hence oxygen is essential to stabilise single metallic films.

For powder metallurgical foams a minimum amount of oxides is necessary to stabilise foams, which also strongly influences the maximum expansion (Weigand (1999)). Other studies postulated that cell wall surfaces covered by dense oxide layers support or are even required to stabilise aluminium foams (Dudka et al. (2008), Babcsán et al. (2004), and Leitmeier et al. (2002)). Now these theses can be supported by an exact value of the required oxygen content, which is suspected to be essential for stabilising Al foams made of the same melts.

Beside the necessity of a minimum oxygen content it was found, that the more particles are added, the less oxygen is required, which can be called an effect of particle stabilisation. How stabilisation exactly works in this case is difficult to determine because it is unknown how the particles behave in a liquid. One reason could be the viscosity increase caused by the addition of solid particles. For 20 vol.% SiC particles in an AlSi6.5 alloy, the viscosity will be enhanced to 25 times the original value (2 mPas to 50 mPas) (Flemings (1991)).

We suspect that particles are captured by the oxygen layer and cannot further move, thus reducing the mobility of the surface, which in turn stabilises the film. Ip et al. also demonstrated that particles that are not totally wetted tend to stay at the solid-gas surface, modify the curvature of the Plateau border and influence capillary suction (Ip, (1999)).

Variation of the pulling velocity, respectively time up to solidification, reveals that the faster a film gets pulled out, the more oxygen is required to keep it stable. This result was surprising since it seemed valid to assume that a metastable liquid film could be prevented from rupture by fast solidification and thus less oxygen would be required. However, the opposite is true, which can only be explained by the reduced oxidation time of the liquid-gas interface when pulling films fast (10 mm/s). Garcia-Cordovilla et. al. have found that the more oxygen is present, the faster the surface gets totally oxidised, which seems to be similar in our experiments (Garcia-Cordovilla (1986)). Their minimum of 500 ppm O₂ which is required to form a monolayer of oxide is in good agreement to our values. Whether the formation of an oxide layer is totally prevented or it is just not strong enough cannot be answered yet.

It became obvious during our study that oxygen plays a major role in almost every case, like building MgO to increase the viscosity, capturing particles at the solid-gas interface, the oxidation time and especially the necessity of a slight oxygen concentration (>200 ppm) in the atmosphere. Thus we can postulate that oxygen might be the missing link of foam stabilisation.

5. Conclusions

- Films of Mg-free alloys (pure Al and AlSi9) as well as their TiB₂-reinforced composites are less stable than Mg-containing systems.
- The slower films are pulled and the more particles are present, the less oxygen is required to stabilise a film made of AlSi9Mg0.6.
- In oxygen-saturated atmospheres, particles tend to settle along the solid-gas interface and thus inhibit the mobility of the surface. This will prevent films from further thinning.
- Oxygen plays a major role for the stabilization of single films. In an inert atmosphere (10⁻⁸ ppm O₂) no stable films are possible in any case.

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