CHARACTERIZATION OF RAPIDLY SOLIDIFIED METALLIC ALLOYS USING COMBINATION OF EXPERIMENTS AND MODELLING

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ABSTRACT

Most metallic materials are produced from their liquid state. In order to control the properties of industrial products, it is very important to understand their solidification path and the resulting microstructures which can be significantly affected by melt undercooling. High undercooling results in rapid solidification and a refined microstructure with minimal microsegregation. This paper reports on the analysis of rapidly solidified Al-Cu droplets obtained by a single fluid atomization process, Impulse Atomization. A quantitative analysis by Rietveld refinement method of the Neutrons Diffraction data was carried out to determine the fraction of the intermetallic Al_2Cu. Knowing the fraction of Al_2Cu, the eutectic fractions and corresponding dendritic and eutectic undercoolings were estimated using the metastable extensions of solidus and liquidus lines of the Al-Cu system calculated by Thermo-Calc. In addition to this work, a model of microsegregation coupled with ThermoCalc software via TQ (application programming interface of ThermoCalc) and the Wang-Beckerman model for dendritic growth velocities has been developed for binary alloys. This has led to the development of a phenomenological relationship between primary phase undercooling and initial growth velocity. A comparison of estimated primary undercoolings using a coarsening model with the adiabatic undercoolings for each alloy composition has confirmed that solidification occurs under adiabatic conditions during recalescence.

KEY WORDS

Impulse Atomization, Rapid Solidification, Aluminum-Copper, Undercooling, Microsegregation, Neutron Diffraction, Thermodynamic equilibrium calculations, Coarsening, Growth velocity, Recalescence

INTRODUCTION

Manufacturing of most metallic alloys products involves solidification at some stage. Mechanical properties of those products are generally related to their solidification microstructures. Depending on the final application of a product, a certain type of microstructure is more appropriate compared to another. For a product that requires directional properties, a microstructure of columnar grains is needed while isotropic properties are satisfied with an equiaxed structure. Moreover, it has been found that fine structures with high chemical homogeneity yield a stronger material. Therefore it is important to understand all the dynamics involved in the formation of solidification microstructures in order to control the properties of the final products.

Generally, post-processing of the solidified materials is required to obtain the final product with desired properties. These post-solidification treatments are generally time-consuming and therefore increase the production cost without fully eliminating solidification related defects such as segregation. Thus, efforts have been made towards developing cast to products processing routes such as die-casting and strip casting. In order to control the microstructure in these types of rapid solidification processes, modelling solidification is required in order to shorten the production time, reduce cost and to understand metastable phases that form under these processing conditions. Experimental results are required to validate these numerical models. Therefore, suitable experimental techniques allowing control of the solidification parameters such as cooling rate and undercooling are required in order to achieve sustainable results. Designing such experimental technique is a real engineering issue especially due to the requirement of heat transfer from the solidifying system to its environment. For decades, the most widely used experimental technique to generate benchmark data for numerical simulations has been the Bridgman type of directional solidification (Miller & Pollock 2014). This technique allows the independent control of essential solidification parameters namely the alloy initial composition, the temperature gradient and the growth rate. However, Bridgman type solidification experiments cannot achieve solidification rates high enough to compare with the solidification structures resulting from rapid crystallization processes such as strip casting, rheo-casting and spray deposition where high cooling rates and high undercoolings induce vast deviation from equilibrium during solidification. Dendrite growth from an undercooled melt depends a great deal on the nucleation undercooling. Therefore, determination of undercooling and the resulting growth rate, recalescence, microsegregation / phase fraction and grain size is very important.

The Electro-Magnetic Levitator (EML) has been the only experimental approach to allow for direct measurements of dendritic undercooling and growth velocities using a pyrometer and a high speed video camera to observe the solid-liquid interface displacement (Herlach, Galenko & Holland-Moritz, 2007) (Ilbagi et al, 2011). It has enabled these measurements to be carried out on a wide range of alloy systems due to its ability to melt and solidify samples in a containerless environment. The EML method is restricted to one measurement of growth velocity versus undercooling per experiment. As the size of the levitated samples in an EML setup is of the order of 6 mm, only a portion of the solidified sample undergoes rapid solidification. This makes microstructural examination of the rapidly solidified portion very difficult to isolate. Recently, dedicated efforts have been made to develop microstructure selection maps using containerless solidification technique such as a drop tube (Norman et al, 1998) (Zamboni et al, 1998). More recently, efforts to quantify phase fractions, including, developments of numerical models based on microsegregation during rapid solidification of a dendrite from a single nucleation point which were validated by experimental results obtained from rapid solidification of liquid droplets generated by containerless techniques such as Impulse Atomization (Henein, 2002) (Tourret & Gandin, 2009, 2011) (Prasad, Mosbah, Henein & Gandin, 2009). This technique provides more control over solidification parameters such as cooling rate, undercooling and growth rate. During IA large undercoolings can be achieved since heterogeneous nucleation on container walls is avoided (Prasad, 2006). Moreover, since many droplets of different sizes are often obtained, different undercoolings and cooling rates can be analyzed, cooling rate being directly related to the droplet size and the cooling gas under which the atomization takes place (Wiskel, Navel, Henein & Maire, 2002). However, due to experimental difficulties, in-situ measurements of growth velocity and undercooling are yet to be achieved. But recently, it has been

possible for us to experimentally quantify the dendritic and eutectic undercoolings during rapid solidification of Al-Cu droplets by combining the weight percent intermetallic Al_2Cu obtained by Rietveld refinement analysis of neutron diffraction results with data from the metastable extension of the solidus and liquidus line of Al-Cu phase diagram using ThermoCalc. These results were then used to validate a microsegregation model of binary alloys solidification which gave us not only eutectic fractions in agreement with the experimentally obtained values but also dendrite growth rates corresponding to the measured undercoolings.

The objective of this work is to show that single fluid atomization techniques coupled with mathematical modelling can be used as valuable tools to generate solidification data of undercooling and growth velocities under rapid solidification conditions. The microsegregation model in which growth rate determination is based on the model proposed by Wang and Beckermann (1993) will then be run for the same undercoolings with constant values of growth rates so as the output result gives the experimental value of eutectic fractions. Thus a phenomenological relationship between undercooling and growth velocity can be developed and compared with the Lipton, Kurz and Trivedi (LKT) model (Lipton, Glickman & Trivedi, 1987). LKT model is an extension of the Lipton, Glickman and Kurz (LGK) theory (Lipton, Glickman & Kurz, 1987) for high growth rate. Both models are developed based on the stability analysis of a moving solid-liquid interface during solidification of a dilute binary alloy. These models were found to be in good agreement with experimental velocity-undercooling results (Willnecker, Herlach & Feuerbacher, 1989). The advantage of having such a velocity-undercooling function is not only to avoid the use of EML experiments but also the methodology could be extended to low-temperature and multi-component alloys such as D2 steel.

METHODOLOGY

Droplets production by Impulse Atomization (IA)

Al-Cu of three compositions (wt% Cu: 5, 10 and 17) were produced by IA under Helium (He) and Nitrogen (N_2). These droplets were already well analyzed in our previous papers. Table 1 summarizes the alloys compositions, droplet sizes and atomization gas used in the present paper (Prasad et al, 2009) (Bogno, Khatibi, Henein & Gandin, 2013).

Table 1- IA Al-Cu droplets of different compositions and sizes atomized from 1123K in N_2 and He

Alloy Composition	Atomization gas	Droplet Size (μm)
Al-5wt% Cu	He	196
		925
	N_2	196
		925
Al-10wt% Cu	He	196
		925
	N_2	234
		925
Al-17wt% Cu	He	196
		925
	N_2	234
		780

Quantification of primary and eutectic undercooling

Determination of both the primary and the eutectic nucleation undercoolings was achieved using neutrons diffraction (ND) data, the extension of solidus and liquidus lines of the Aluminum rich hypoeutectic region of Al-Cu phase diagram by ThermoCalc (Figure 1) and an approximate coarsening model proposed by Kurz & Fisher (1998). The procedure, described in details by Prasad et al (2009) and in a keynote paper (Bogno et al, 2013), consists in (i) Estimating the eutectic fractions (from the weight percent intermetallic Al_2Cu obtained from rietveld refinement of ND data) from the extended solidus and liquidus lines (metastable phase diagram) and the use of Gulliver-Scheil predictions (ii) Obtaining the corresponding eutectic nucleation temperature (and therefore the eutectic nucleation undercooling) from the metastable phase diagram and finally (iii) Using a coarsening model and assuming that most of the primary solid phase form during coarsening, the primary nucleation undercooling is determined.

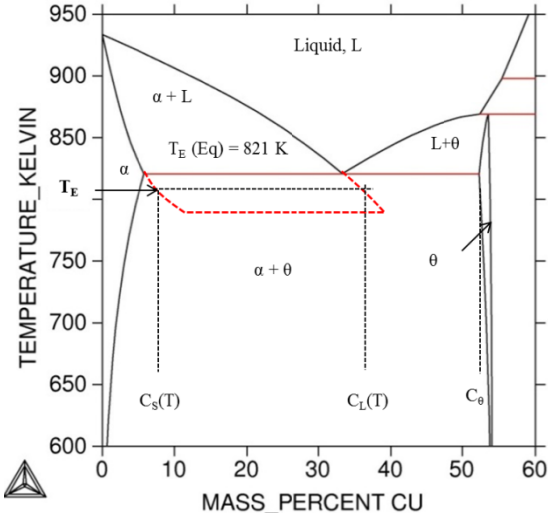

Figure 1: Aluminum rich hypoeutectic region of Al-Cu phase diagram calculated by Thermo-Calc. The dashed lines represent the extension of solidus and liquidus lines obtained by suspension of Al_2Cu

RESULTS AND DISCUSSIONS

Experimental results

Table 2 summarizes the experimental results pertaining to the three investigated alloys. A detail description of the way these results were obtained is described elsewhere (Bogno et al, 2013). The primary and eutectic undercooling values for each droplet are used as input variables to run a solidification microsegregation model of a binary alloy droplet falling through a stagnant gas (Tourret & Gandin, 2009, 2011). It can be seen from Table 2 that for a given alloy composition, the primary and eutectic undercoolings are quasi-constant in the range of droplets size /cooling rates studied so that for each composition an average value of the undercooling could be used.

Table 2 – Summary of the experimental results for the three investigated Al-Cu alloys

Alloy composition	Atomization Gas	Droplet size (μm)	Eutectic fraction (wt.%)	Eutectic undercooling (K)	Dendritic undercooling ΔT_C (K)
Al-5wt% Cu	He	196	7.53	20.9	38.7
		925	7.62	20.0	38.1
	N_2	196	7.92	17.3	36.1
		925	7.88	17.6	36.4
Al-10wt% Cu	He	196	15.6	29.0	98.7
		925	15.4	29.5	99.2
	N_2	234	19.8	14.6	84.9
		925	16.7	25.4	95.2
Al-17wt% Cu	He	196	29.3	34.9	79.5
		925	31.7	30.4	77.3
	N_2	234	30.9	32.3	76.2
		780	30.9	32.2	76.1

Model's prediction

Primary phase and recalescence

The values of undercooling shown in Table 2 are entered as variable inputs into the microsegregation model. The output results of the model give several solidification parameters such as solidification time, cooling rate, growth velocity and fraction of primary solid phase formed during the period of recalescence. Wiskel et al (2002) reported that for two droplets of the same size, solidification is faster for a droplet atomized in He as compared to the one atomized in N_2. And, for two droplets of different sizes atomized in the same gas, the smaller droplet solidifies faster. In a previous work, we have also analyzed and compared the solidification time during the period of recalescence with the duration of coarsening. The result showed that the time fraction during recalescence (0.2 to 23 % of total primary solidification time) is negligible as compared to the duration of coarsening so that most of the primary solid phases form during coarsening as shown in Figure 2. The use of a coarsening model to estimate the primary undercooling is thus justified.

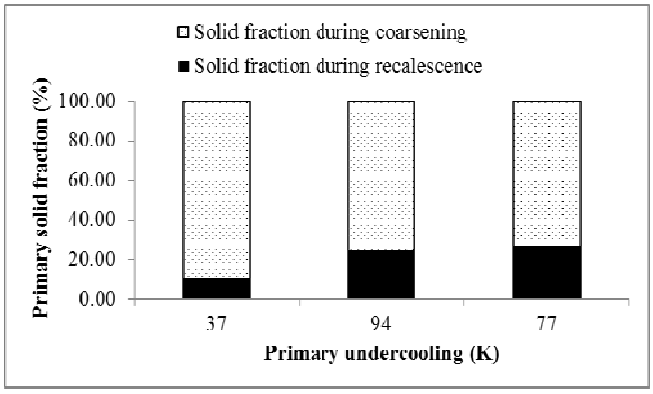

Figure 2: Fraction of primary solid phase formed during the periods of recalescence and coarsening for three average values of undercooling corresponding to the three investigated alloys

In an undercooled droplet, if the primary phase formation happened at a rate sufficiently fast relative to the time required for heat exchange with surrounding gas, an overall adiabatic condition could be established between a droplet and the stagnant surrounding gas. Assuming that after a droplet has undercools by ΔT, nucleation occurs, recalescence will follow. During the period of recalescence if solidification occurs under adiabatic conditions, then the adiabatic undercooling temperature, ΔT_A, can be determined from the solid fraction F_R formed during recalescence (determined using the microsegregation model) using equation (1)

$$\Delta T_A = F_R \,.\, \Delta T_{hyp} \tag{1}$$

The characteristic undercooling/hypercooling limit ΔT_{hyp} of the melt is given by

$$\Delta T_{hyp} = \frac{\Delta H_f}{C_p^l} \tag{2}$$

Where C_p^l is the melt heat capacity and ΔH_f the latent heat of fusion.

Table 3- Thermal properties of the three alloys under investigation (Tourret et al, 2011)

Property	Al-5wt.% Cu	Al-10wt.% Cu	Al-17wt.% Cu
C_p^l (J.m^{-3})	3.25×10^6	3.31×10^6	3.40×10^6
ΔH_f (J.m^{-3})	1.09×10^9	1.13×10^9	1.18×10^9
ΔT_{hyp}	335	340	348

The hypercooling values, ΔT_{hyp} of the three alloy compositions are given in Table 3 as well as the the melt heat capacity C_p^l and the latent heat of fusion ΔH_f .

In Figure 3, the adiabatic undercooling, ΔT_A, is compared with the coarsening undercooling, ΔT_C. As can be seen a fairly good agreement is found between the calculated average values of adiabatic undercooling (ΔT_A) for each alloy composition and the ones estimated using the coarsening model (ΔT_C). However, the nucleation undercooling values (77K) corresponding to Al-17wt% Cu are found to be not

fitting the x = y curve. This stems from the fact that during atomization of this particular alloy the oxygen level was for some reasons 500 ppm which is very much high as compared to 20 ppm prevailing during atomization of the two other alloys (5wt% Cu and 10wt% Cu). Thus, the experimental values of nucleation undercooling for Al-17wt% Cu were affected by the oxygen level in the atomization tower.

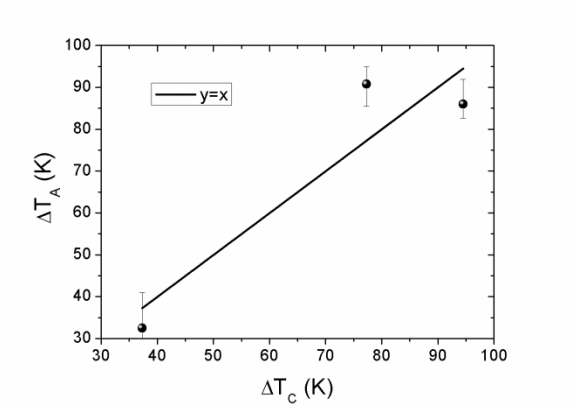

Figure 3: Comparison of calculated average values of adiabatic undercooling (ΔT_A) with the estimated values using the coarsening model (ΔT_C) for each alloy composition

Growth velocity

Initial growth velocity variation with primary undercooling is plotted for the three investigated alloys in Figure 4. The resulting curves show that initial growth velocity increases with primary undercooling. This is in agreement with results obtained from EML (Herlach et al, 2007).

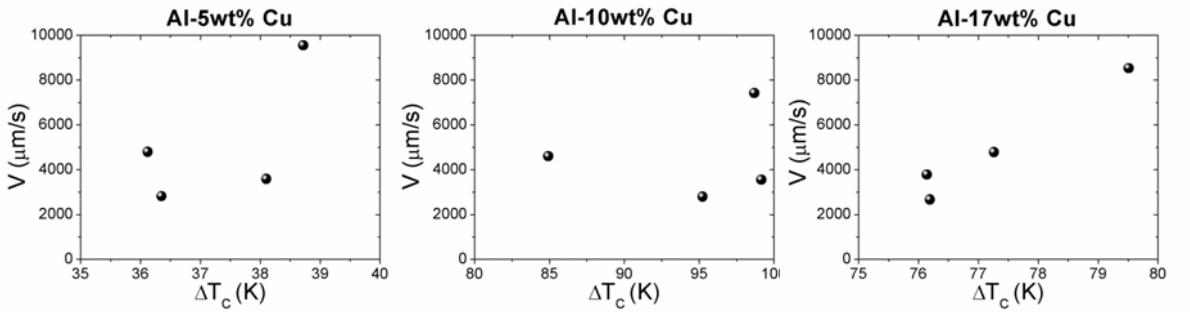

Figure 4: Initial growth velocity variation with primary undercooling for the three investigated Al-Cu alloys

CONCLUSIONS

In this work, we proposed Impulse Atomization (IA) as a controlled experimental technique capable of full characterization of highly undercooled rapidly solidified alloys. A model alloy, Al-Cu of different compositions was atomized and the resulting droplets of different cooling rates and undercoolings were investigated. Primary dendritic and eutectic undercoolings were estimated using a combination of neutron diffraction data, the metastable extension of solidus and liquidus lines of the phase diagram using ThermoCalc and a coarsening model. The experimental results were then used to validate a model of microsegregation for binary alloys that predict characteristic variables involved in rapid solidification microstructures formation such as the eutectic fraction and dendrite growth velocity as a function of undercooling. The results suggest that it is possible to develop a phenomenological relationship between growth velocity and undercooling so that not only experimental techniques such as EML could be avoided but also growth velocities for low-temperature and for multi-component alloys could be predicted.

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