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DENDRITE REFINEMENT OF AL_9Co_2 COMPOUND BY A CONTINUOUS INCREASE OF THE COOLING RATE DURING SOLIDIFICATION

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O modificare continuă a vitezei de răcire la solidificare a fost aplicată unui aliaj hypereutectic Al-9.71% at.Co conținând dendrite primare de compus Al_9Co_2, de interes ca precursor pentru obținerea de catalizatori tip Raney-Co. O gamă a vitezelor de răcire la solidificare cuprinzând aproape cinci ordine de mărime a fost asigurată printr-un dispozitiv de turnare tip probă-pană cu cochilă de Cu. Muchia extrem de ascuțită a probei-pană din dispozitivul conceput (semi-unghi la vârf α~4°) a asigurat o semi-grosime a vârfului probei-pană de ~50µm şi o viteză de răcire apropiată de cea obținută prin tehnicile de solidificare ultrarapidă. Micrografiile optice înregistrate de-a-lungul înălțimii probei-pană au indicat o micşorare a dimensiunii dendritelor de compus Al_9Co_2 la scăderea grosimii probei-pană, după o dependență care apărea neliniară. Această neliniaritate a fost raționalizată prin modelarea probei-pană având geometria şi dimensiunile utilizate, pe baza unui parametru termic-geometric $H_i = D_c^{1.5}/D_m^{0.15}$ care ia în considerare atât grosimea peretelui cochilei (care acționează ca absorbant de căldură) cât şi grosimea aliajului lichid (care acționează ca sursă de căldură în schimbul termic de la interfață).

Continuous modification of the cooling rate during solidification has been applied to a hypereutectic Al-9.71at.%Co alloy comprising Al_9Co_2 primary dendrites that may be used as a precursor for making Raney-Co catalysts. A range of cooling rates of about five orders of magnitude have been achieved by means of a "wedge-shape copper mould device". The extremely sharp edge of the wedge-shape casting (half apex angle α ~4°) has ensured a very thin half-thickness of the casting at its sharp edge (~50µm) and a cooling rate comparable to that achieved by rapid solidification techniques. The various optical micrographs recorded along the height of the wedge-shape castings have pointed to a decrease in size of the Al_9Co_2 dendrites as the casting thickness decreased, that seemingly manifested a non-linear dependence. This non-linearity was rationalized by modeling the "wedge-shape mould and casting" device used in the experiment on the basis of a thermal-geometrical parameter $H_i = D_c^{1.5}/D_m^{0.15}$ that takes into account both the mould wall thickness (acting as a heat sink) and the liquid alloy thickness (acting as a heat source) in the heat transfer at the interface.

Keywords: Al_9Co_2, wedge-shape mould/casting device, dendrite size refinement

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1. Introduction

Various cobalt-aluminides (Al_9Co_2, $Al_{13}Co_4$, Al_5Co_2, AlCo) may appear in the microstructure of cast Al-Co alloys depending on alloy composition [1]. If the aluminides have a dendrite morphology and the dendrite size is small enough, the Al alloys comprising the aluminides may be used as precursors for making cobalt skeletal catalysts [2]. Such Co-Raney catalysts are less active but more selective than the corresponding Ni-skeletal catalysts.

The importance of fine dendrite size of the aluminide compound in the precursor Al-TM alloy (TM=a transition metal,- Co,Ni,Cu-) is related to the fact that skeletal TM catalysts are obtained by subjecting the precursor Al-TM alloy to an alkali leaching process when a selective dissolution of Al takes places leaving a spongy TM structure with high specific area and high catalytic activity [3-5].

Raney-Co catalysts are made by alkali leaching of an Al-Co alloy, whose Co content is either 35-40wt%Co or 49wt%Co (the last composition being the most widely used). In such precursors various Al-rich aluminide compounds (Al_9Co_2, $Al_{13}Co_4$, Al_5Co_2) exists which are activated during the selective dissolution of Al. In a previous paper [6] we have investigated an Al-Co alloy comprising the aluminide that is richest in Al, namely Al_9Co_2 for which we have demonstrated a dendrite morphology whose size was dependent on the cooling rate applied during solidification. Because rapid solidification is nowadays considered to be a new route for producing fine dendrites in Al-TM precursors for making skeletal catalysts [7,8], in our previous paper [6] we have investigated the dendrite size of Al_9Co_2 compound in an Al rich hypereutectic Al-Co alloy (9.71at%=15.82wt%) solidified at two extreme cooling rates, namely ~5 $^oC/s$ when the alloy was die cast and ~$5x10^6$ $^oC/s$ when the alloy was rapidly solidified by melt-spinning.

In this paper we go further with the investigation of the same alloy and we study the microstructures obtained by applying intermediate cooling rates modified in a continuous manner by using a wedge-shape copper mould. Actually for skeletal Ni catalysts (RQ Ni) prepared by alkali leaching of rapidly quenched Ni–Al alloys, systematic studies have been performed, focusing on the effect of variable cooling rate during alloy preparation [9]. It was found that the residual Al content, texture, structure, surface hydrogen species, and active sites of the Ni catalysts can be controlled by the cooling rate of the Ni–Al alloys.

2. Experimental

The wedge-shape mould method is common practice for investigating the structural modifications in cast iron, but it has rarely been used for non-ferrous alloys. At our knowledge it has not been used as yet to investigate the dendrite size refinement in Al based alloys. Instead it has been applied to study the competitive formation of stable and metastable phases in the Al-Ge alloy system [10]. As pointed out in this paper at high cooling rates the wedge-shape mould method gives local cooling rates that are more reproducible than those obtained when using other rapid solidification techniques (melt-spinning, melt extraction). At intermediate cooling rates the wedge-shape mould method provides a very large range of cooling rates.

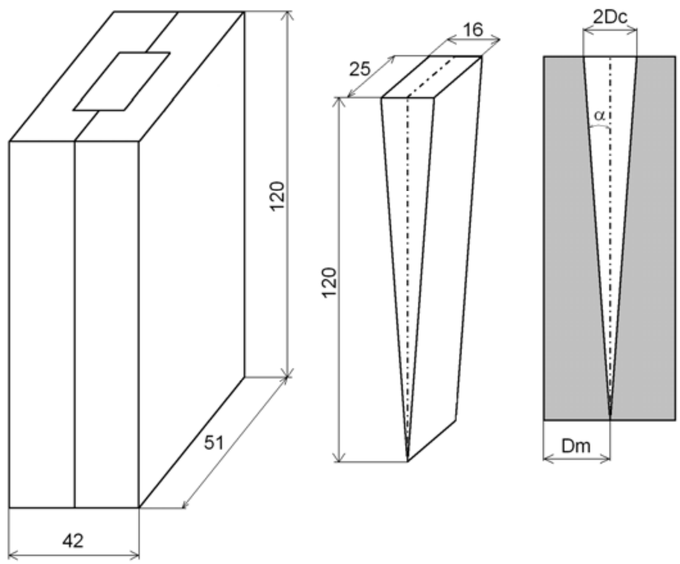


Fig.1 Schematic depiction of the wedge-shape copper mould-casting device used to give a range of cooling rates during solidification (the dimensions are in millimetres); the two halves of the copper mould; the wedge-shape Al alloy casting; vertical cross section through the wedge-shape "mould-casting device'

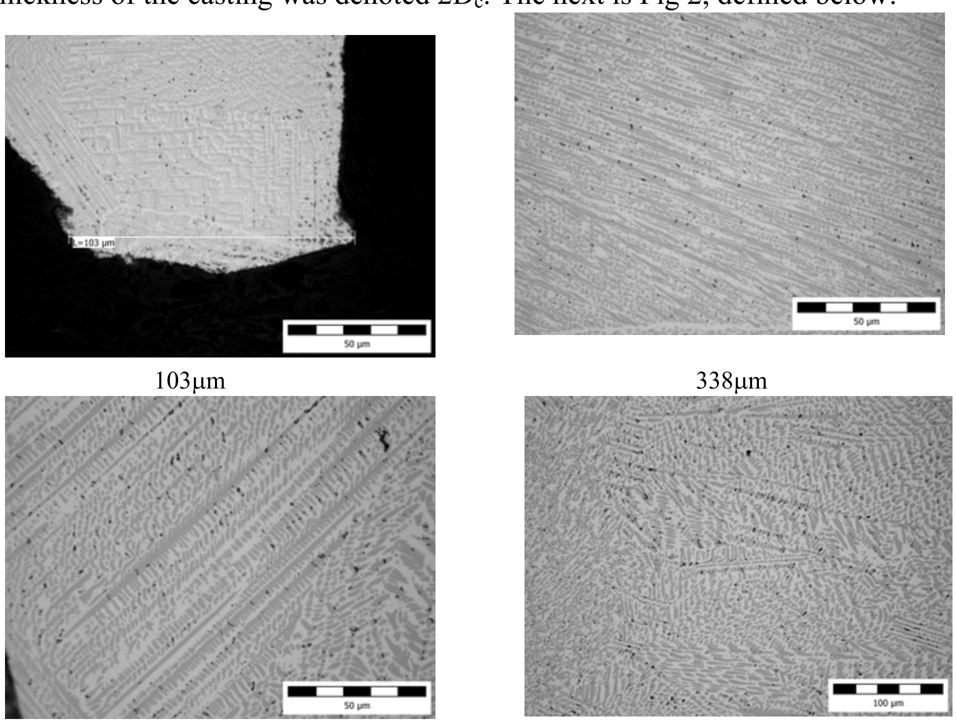
For the purpose of this paper we have conceived a wedge-shape copper mould with the geometry and dimensions depicted in Fig.1.

3. Results

The wedge-shape casting (Fig.1b) obtained after solidification of the liquid alloy was easily taken out from the copper mould by simply detaching the two halves of the mould as indicated in Fig.1a.

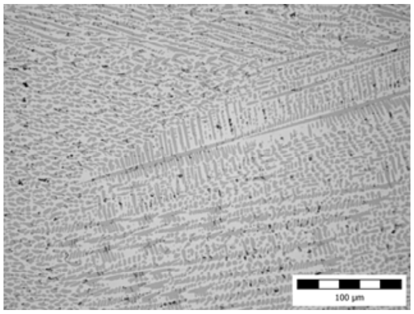
The wedge-shape casting of 25 mm depth (Fig.1b) was first cut along a vertical cross-section for obtaining two thinner similar halves (12.5 mm depth). One half was kept for other type of investigations, while the second was used for microscopic investigation. The vertical triangular face of the front half of the wedge-shape casting intended to be used for microscopic investigation (Fig.1b) has been in direct contact with the mould wall and it was just on this face that the microscopic study was conducted. Because the height of the wedge-shape casting intended to be used for optical microscopic investigation was too large (120 mm) it was cut along its height (from top to bottom) into 5 smaller samples, each one 24 mm height. Each sample was embedded in synthetic resin, the face that has been in contact with the mould wall being set in the "up" position, ready to be prepared for microscopic examination. The samples were polished and etched with Keller etchant. An optical microscope was used for recording the micrographs.

For each sample several micrographs have been recorded as close as possible to the border. The exact location of the micrograph was specified by indicating the thickness of the casting in the given position. Given the symmetry of the wedge-shape casting with respect of the vertical axis (see Fig.1b) the thickness of the casting was denoted $2D_c$. The next is Fig 2, defined below:



103µm 338µm

708µm 1534µm



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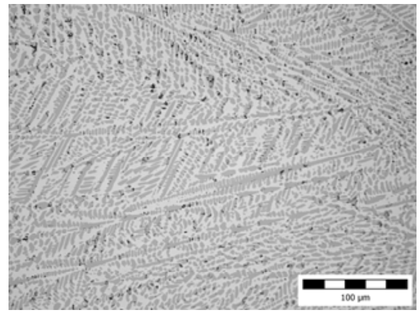

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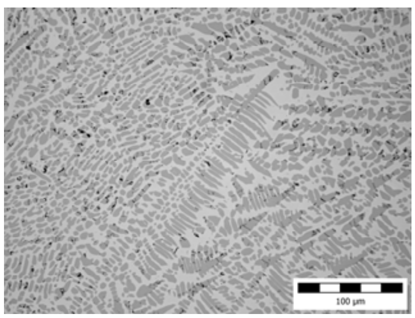

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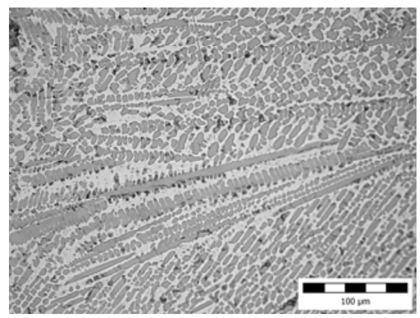

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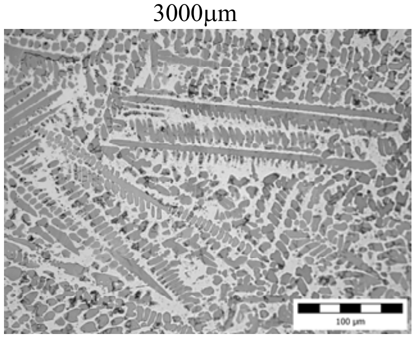

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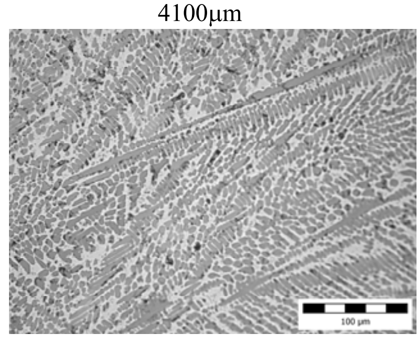

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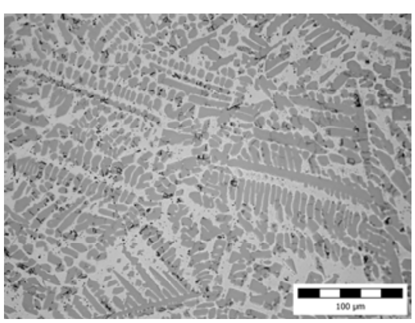

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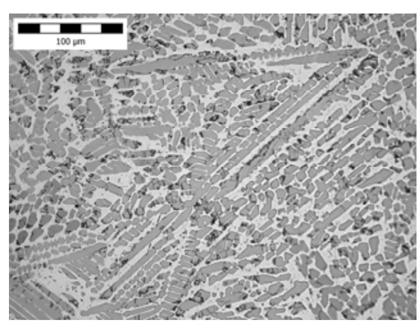

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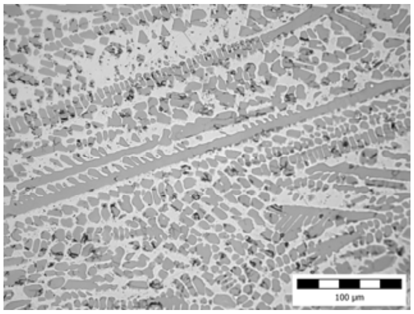

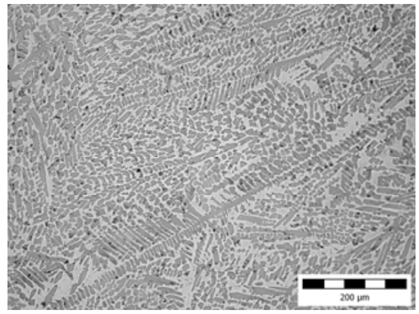

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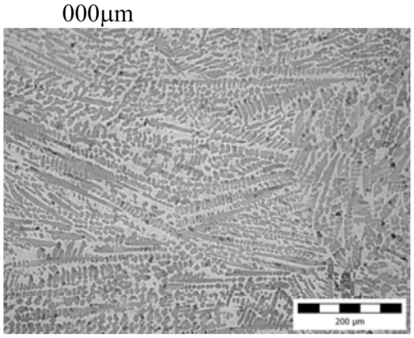

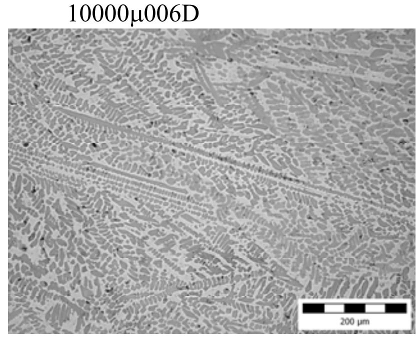

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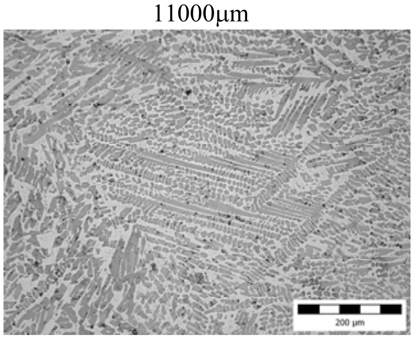
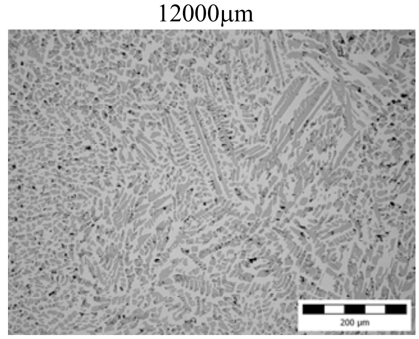
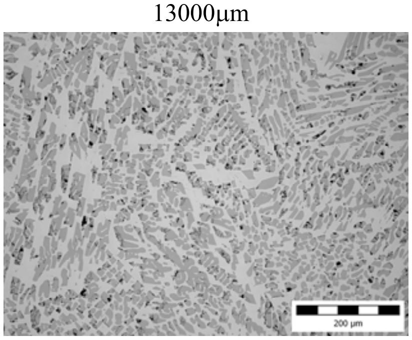
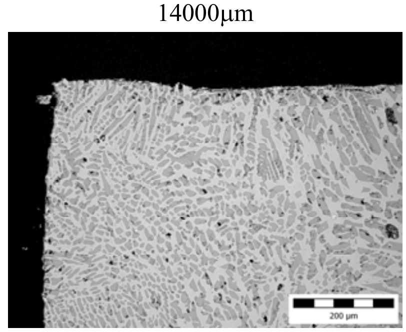




13000μm 14000μm





15000μm 16000μm

Fig. 2 represents a series of optical micrographs recorded from bottom to top of the wedge-shape casting at various locations specified by the value $2D_c$

The $2D_c$ decreased gradually from top to bottom from 16 mm to theoretically zero (at the sharp edge of the wedge-shape casting). The series of micrographs in Fig.2 have been recorded along the height of the wedge-shape casting at positions equally apart with respect to $2D_c$.

4. Discussion

As one can see in the series of micrographs in Fig.2 when increasing $2D_c$ the size of the dendrites of the Co_9Co_2 compound increases gradually on account of a continuous decrease in the cooling rate during solidification. Two decades ago Flemings [11] has demonstrated that for a series of Al base alloys increasing the cooling rate diminishes the solidification time t (in seconds) and consequently diminishes the spacing d (in micrometers) between the secondary dendrite arms, according to a relationship that for the investigated alloys takes the form:

$$d=7,5\ t^{0,39} \qquad (1)$$

The range of cooling rates achievable in our device may be estimated by considering in Fig.1c $\tan\alpha=D_c/h=0.06667$, hence $\alpha=3^o50'$ and $2\alpha=7^o\ 40'$. On account of this extremely low value for angle 2α, the value $2D_c$ is extremely low at the sharp edge of the wedge-shape casting (~100 μm as seen in the first micrograph in Fig.2). In comparison with the thickness of rapidly solidified melt-spun ribbons (estimated to be ≤ 50 μm) the thickness D_c of the half of the thin edge of our wedge –shape casting (that was in contact with the copper mould wall, -see Fig.1c) is about the same (50 μm). So one may infer that at the bottom sharp edge of our wedge-shape casting the cooling rate will be extremely large, of the same order of magnitude as the one achieved in melt spinning or in other rapid solidification techniques ($\leq 10^6$ $^oC/s$).

On the other hand at the top end of our wedge-shape casting the cooling rate is typical for a 16x25 mm sample consisting in an Al base alloy cast in a rectangular copper mould whose wall thickness is 13 mm (~10 $^oC/s$),- see Fig.1a.- So a span of about five orders of magnitude in the cooling rate is achievable in our wedge-shape experimental device.

As stated above in the series of micrographs in Fig.2 the size of the dendrites was correlated with the thickness $2D_c$ of the wedge-shape casting. Indeed $2D_c$ was easy to be measured on the polished surface of the sample. On the other hand it is reasonable to admit that increasing $2D_c$ (from 102μm at the bottom sharp edge of the wedge-shape casting up to 16000μm at the top largest thickness of the casting) increases the solidification time and consequently decreases the cooling rate.

Unfortunately specifying $2D_c$ is not entirely relevant for the heat transfer conditions and consequently for the cooling rate prevailing at each location of the microstructure. Indeed to specify the thermal regimen at the interface between mould and casting one has to take into consideration that in the heat transfer process the liquid alloy acts as a heat source and the copper mould acts as a heat sink. Hence both the casting thickness and the mould wall thickness D_m have to be considered for a proper characterization of the thermal regimen at a given location. Such a specification can be made by means of a more complex thermal-geometrical parameter H_i defined by the following expression in the paper of Prabhu et al.[12]

$$H_i = D_c^{1.5} / D_m^{0.15} \tag{2}$$

For an Al-Cu-Si alloy (LM-21) Prabhu and his co-workers have performed both computer modelling of the heat flow [13] as well as experimental measurements of thermal parameters [12]. In so doing Prabhu and his co-workers have put in evidence the physical significance of parameter H_i in the heat transfer during the solidification process by correlating it with the local time of solidification. The local solidification time for the alloy under consideration is defined as the time required for a given fixed location in the casting to go from the liquidus temperature to the solidus temperature and it is in inverse ratio with the cooling rate imposed at this definite location. Fig.3a depicts the linear correlation between the local solidification time and the geometrical parameter H_i , as obtained in [12] for an Al-Cu-Si alloy. Moreover for the same alloy the local solidification time was correlated with the dendrite arm spacing (Fig.3b).

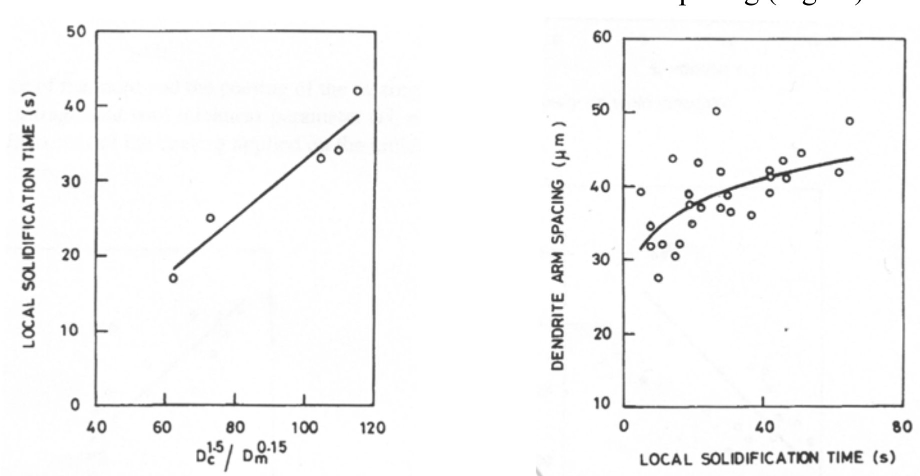


Fig.3 Influence of the geometrical parameter H_i on the solidification process of an Al-Cu-Si alloy (LM-21), reproduced from [12]

In Fig. 3 there are represented: a) variation of the local solidification time with H_i and b) effect of local solidification time on dendrite arm spacing DAS.

In order to model our wedge-shape mould/casting device with respect to H_i we have represented in Fig.1c a vertical cross-section through the device having the geometry and dimensions used in our experiment. On account of the symmetry of the device only one half has to be considered, for instance the left half and so in relationship (2) we have to consider only half of the casting thickness $2D_c$, namely D_c. Figure1c shows that not only D_c varies along the height of the casting but D_m is also variable from bottom to top of the mould. From geometrical reasons $D_m = 21-D_c$ (all dimensions in mm). So for the particular configuration of our wedge-shape mould/casting device we have derived an equation for the dependence of H_i on D_c as follows:

$$H_i = (D_c)^{1.5} / (21-D_c)^{0.5} \qquad (3)$$

Table 1

Geometrical parameter H_i calculated in function of D_c for the "wedge-shape mould and casting device" used in the experiment

$2D_c$	D_c	$D_m = 21-D_c$	$Hi = D_c^{1.5} / D_m^{0.5}$	$H_i / 2D_c$
16	8.0	13.0	6.2757	0.3922
15	7.5	13.5	5.5902	0.3727
14	7.0	14.0	4.997	0.3536
13	6,5	14.5	4.3520	0.3348
12	6.0	15.0	3.7947	0.3162
11	5.5	15.5	3.2762	0.2974
10	5.0	16.0	2.7951	0.2795
9	4.5	16.5	2.3500	0.2611
8	4.0	17.0	1.9403	0.2425
7	3.5	17.5	1.5652	0.2236
6	3.0	18.0	1.2247	0.2041
5	2.5	18.5	0.9190	0.1838
4	2.0	19.0	0.6489	0.1622
3	1.5	19.5	0.4160	0.1387
2	1.0	20.0	0.2236	0.1118
1	0.5	20.5	0.0781	0.0781
0.5	0.25	20.75	0.0274	0.0540
0.25	0.125	20.875	0.0097	0.0387
0.10	0.05	20.95	0.0024	0.0240

In table 1 we have calculated the values of the geometrical parameter H_i by introducing in eq.(3) the values D_c at which the micrographs in Fig.2 have been recorded. Fig.4 is the graphical representation of the pair of values H_i and $2D_c$ in Table 1. What's remarkable in Fig.4 is the non-linear dependence between H_i and

$2D_c$. This non-linearity is very pronounced as one can see by examining the decrease in the slope of the graph as indicated by the ratio $H_i/2D_c$ in Table 1.

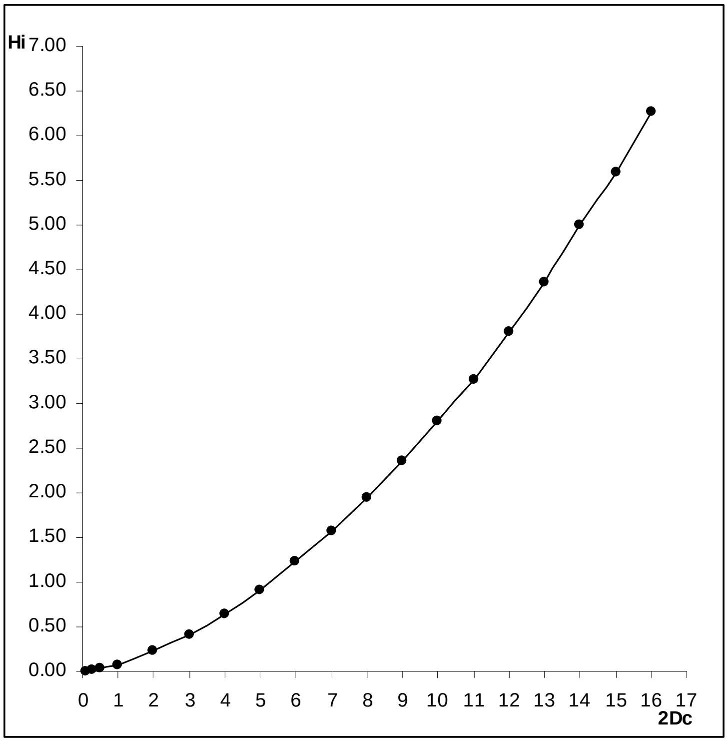


Fig.4. Graphical representation of eq.(3) showing the dependence between H_i and $2D_c$ in the wedge-shape mould /casting device used in the experiment

This non-linearity has a strong meaning in the interpretation of the series of micrographs in Fig.2 with respect of the dendrite size of the Al_9Co_2 compound. First it is worth to notice that the series of micrographs in Fig.2 are recorded at different magnification as indicated by the length bar on each micrograph. Indeed the first three micrographs are recorded at the highest magnification, the following three ones at an intermediate magnification and the remaining ones at the lowest magnification. As expected from the non-linearity of the graph in Fig.4 at low value of the geometrical parameter H_i (the first micrographs in Fig.2, extremely thin liquid alloy thickness $2D_c$) the dendrite size is not very different when increasing $2D_c$, while in the last micrographs in the series in Fig.2 (high value for the geometrical parameter H_i, large alloy thickness $2D_c$) the dendrite size is strongly influenced by increasing $2D_c$.

The main conclusion of the interpretation of our results is that the geometrical parameter H_i (which is very easy to calculate) is a very useful tool for evaluating the local solidification time as well as the cooling rate and consequently the dendrite size in an alloy solidified at different cross-section of the casting. This is true for comparative studies when the alloy and its thermo-physical properties are the same. In such an instance we consider that the geometrical parameter H_i may be considered to be a true thermo-geometrical parameter of great significance in the solidification process.

To verify in a quantitative manner the influence of parameter H_i on the size of the dendrites of the Al_9Co_2 compound, evaluation of DAS by image analysis are in progress and the results will be published in a next to come paper.

5. Conclusions

A wedge-shape copper mould /casting device has been built which provides extremely high cooling rates at the thin edge end of the casting. These cooling rates are comparable to the ones obtained in rapid solidification techniques ($\leq 10^6$ $^oC/s$) due to the extreme small half-thickness of the casting in this region (~50μm). At the same time this wedge-shape copper mould /casting device provides a range of cooling rates of about 5 orders of magnitude from the bottom thin edge end of the wedge-shape casting up to its top, where the cooling rate is typical for a die cast casting.

In a qualitative estimation, the dendrite size of the Al_9Co_2 compound in the investigated Al-Co alloy decreased gradually from the thin edge end of the wedge-shape casting to its thickest top end, in a non-linear manner.

An explanation for this non-linear dependence between dendrite size and casting thickness $2D_c$ was found by calculating a geometrical parameter $H_i = D_c^{1.5} / D_m^{0.15}$ for the wedge-shape copper mould /casting device. For comparative studies involving the same alloy this geometrical parameter (that is easy to calculate) is representative for the thermal regimen at each location along the height of the wedge-shape casting because it takes into consideration both the liquid alloy thickness (that acts as a heat source) as well as the mould thickness (that acts as a heat sink).

Further investigations intended to explain in a quantitative manner the non-linearity between H_i and casting thickness are in progress by applying image analysis for dendrite size measurements in the same alloy.

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