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INFLUENCE OF RAPID SOLIDIFICATION ON THE MICROSTRUCTURE OF ALUMINIUM RICH HYPEREUTECTIC Al-Co ALLOYS

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Un aliaj hipereutectic din regiunea bogată în Al a sistemului Al-Co cu compoziția 9.71%at.Co a fost selectat în intervalul de compoziții în care compusul Al_9Co_2 *cristalizează direct din topitură fără implicarea reacției peritectice. Aliajul a fost solidificat cu două viteze de răcire, și anume ~5x10*^{6} *^{o}C/s obținută prin melt spinning și ~5^{o}C/s la solidificarea în cochilă. Prin difracție de raze X s-a idendificat prezența fazelor de echilibru (Al-cfc și* Al_9Co_2 *–monoclinic) indiferent de viteza de răcire, fără faze metastabile induse de solidificarea ultrarapidă. Examinarea prin microscopie electronică SEM a indicat o morfologie dendritică pentru cristalele primare* Al_9Co_2 *în ambele condiții de răcire, morfologie care poate fi asociată cu o presupusă valoare scăzută a entropiei la topire a compusului* Al_9Co_2*. Amestecul eutectic (Al+*Al_9Co_2*) amplasat interdendritic a prezentat o morfologie globulară. Finisarea granulației dendritelor primare* Al_9Co_2 *indusă de solidificarea ultrarapidă a fost estimată la ~200 ori, luând în considerare grosimea medie a trunchiului dendritelor de ~100 µm la viteză de răcire lentă și ~0.5µm la răcire ultrarapidă. Morfologia dendritică și finisarea granulației produsă prin solidificare ultrarapidă recomandă aliajul ca un posibil candidat pentru producere de catalizatori scheletați prin dezaliere la leșierea alcalină.*

A hypereutectic alloy in the Al rich region of the Al-Co system having a cobalt content of 9.71at.%Co was selected in the composition range where the Al_9Co_2 *cobalt aluminide crystallizes directly from the melt without involving a peritectic reaction. Two different cooling rates during solidification, namely ~5x10*^{6} *^{o}C/s obtained by melt spinning and ~5 ^{o}C/s obtained by die casting have been applied. X-ray diffraction has ascertained the presence of the equilibrium phases, - fccAl and monoclinic* Al_9Co_2*, - irrespective of the cooling rate applied during solidification. No metastable phases have been produced by rapid solidification. SEM electron microscopy has indicated a dendritic morphology for the primary* Al_9Co_2 *crystals in both casting conditions. This morphology may be associated with a presumed low value of the entropy at melting for the* Al_9Co_2 *compound. The eutectic mixture (Al+*Al_9Co_2*) located in the interdendritic space seemed to have a globular morphology. The grain size refinement of the primary* Al_9Co_2 *dendrites induced by rapid solidification was estimated to be ~200 times by considering the average thickness of the dendrite stems that was ~100 µm at slow cooling rate and ~0.5µm at rapid cooling rate. The dendritic morphology and grain size refinement induced by rapid solidification recommends the alloy as a possible candidate for making Co skeletal catalysts through a de-alloying process by alkali leaching.*

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1. Introduction

Cobalt is not a common alloying element in aluminium because its solid state solubility in Al is disappointingly small, namely 0.0009at% Co according to [1] and reconfirmed in a recent monograph [2]. This low solubility has to be ascribed to large discrepancies between Al and Co for all Hume-Rothery factors governing solid state solubility in alloys, namely valence, electron concentration and especially atomic size. Indeed the difference between the Goldschmidt atomic radii between Al and Co is among the highest (12.6%) when considering the binary Al-based alloy systems. Another feature of the Al-Co system that makes Co an unsuitable alloying element in usual Al-based alloys is the quasi-impossibility to produce Al rich hypoeutectic alloys, because the eutectic composition is very close to pure Al, namely 0.5at% Co, according to the data in Table 1 reproduced from the most reliable reference monograph [2].

However Al-Co alloys richer in Co containing cobalt aluminides have found application for making Co skeletal catalysts [3,4]. Such catalysts (type Raney-Cu, Raney-Ni or Raney-Co) are obtained by subjecting the alloy rich in transition metals aluminides to an alkali leaching process, during which the Al atoms are almost completely taken out from the crystal lattice of the aluminide compound giving rise to a spongy metallic structure presenting a high specific area for catalytic activity.

In this paper and in next to come ones we have been concerned with the influence of the cooling rate during the solidification of Al-TM alloys containing TM aluminides (TM=a transition metal) on the grain size of the aluminide compound. Decreasing the grain size of the aluminide compound is expected to give rise to skeletal catalysts with higher specific area and increased catalytic activity. More specifically in this paper we have focused attention on the influence of rapid solidification on the microstructure of Al rich alloys containing the Al_9Co_2 aluminide type compound.

2. Experimental materials and methods

The aim of this paper was to start a research program concerning the influence of the cooling rate during the solidification process on the grain size of cobalt aluminides mainly intended to be used as raw materials for making skeletal catalysts. As specified in Table 1 the cobalt aluminide that is richest in Al has a stoichiometric composition Al_9Co_2 and it was the one that was investigated in this paper.

According to the data in Table 1 the Al_9Co_2 cobalt aluminide may participate in various amounts in hypereutectic Al-Co alloys in the composition range between 0.5at.% Co (=0.52wt% Co) representing the eutectic composition in reaction (6) in Table1 up to 18.18at.% Co (=32.70wt.% Co) representing the composition of the stoichiometric compound Al_9Co_2. The Al_9Co_2 aluminide may solidify in two distinct ways depending on the composition of the original hypereutectic alloy. Indeed in the composition range 0.5-10.5at.%Co (or 0.52 - 20.41wt%Co) the Al_9Co_2 aluminide solidifies as a primary phase from the hypereutectic melt. In contrast to this in the composition range 10.5 - 18.18at.% Co (or 20.41-32.70wt%Co), besides Al_9Co_2 crystals solidified directly from the melt there are also previous Al_9Co_2 crystals resulting from the peritectic reaction (5) in Table 1. In this paper we have prepared one target alloy in the first group, namely an alloy 9.71at.%Co (=15.82wt.%Co).

Table 1

Special points and zerovariant phase transformations in the phase equilibrium diagram of the Al-Co alloy system

Reaction	Composition, at.% Co	Temp. (^oC)	Reaction type	Reaction current no.
$L\leftrightarrow AlCo+(\alpha Co)$	81.0 78.5 84.4	1400	Eutectic	(1)
$L+AlCo\leftrightarrow Al_5Co_2$	23.8 46.3 28.0	1180	Peritectic	(2)
$L+Al_5Co_2\leftrightarrow Al_3Co$	20.8 27.8 25.6	1135	Peritectic	(3)
$L+Al_3Co\leftrightarrow Al_{13}Co_4$	16.5 25.6 24.0	1093	Peritectic	(4)
$L+Al_{13}Co_4\leftrightarrow Al_9Co_2$	**10.5 24.0 18.2**	**970**	**Peritectic**	**(5)**
$L\leftrightarrow (Al)+Al_9Co_2$	**0.5 0.0009 18.2**	**657**	**Eutectic**	**(6)**
$(\alpha Co)\leftrightarrow(\varepsilon Co)+AlCo$	98.0 ~56.0 ~100	~300	Eutectoid	(7)
$L\leftrightarrow(Al)$		660	Melting	(8)
$L\leftrightarrow(\alpha Co)$		1495	Melting	(9)
$(\alpha Co)\leftrightarrow(\varepsilon Co)$			Allotropic	10)
$L\leftrightarrow AlCo$	50	1640	Congruent	(11)

The detailed composition of the target alloy and the level of all present impurities is given in Table 2, as determined by X-ray fluorescence spectroscopy by means of a SPECTRO XEPOS ED(P)-XLF spectrometer.

The alloy has been prepared by melting pure Al and pure Ni in an induction melting furnace in a graphite crucible. The melt was protected against oxidation by using a flux consisting of an AlF_3 + NaF fluorides mixture. Because of the high difference in specific weight (γ_{Al} =2.70g/cm^3 ; γ_{Co} =8.92g/cm^3) and in melting temperature ($T_{m,Al}$ =660^{o}C; $T_{m,Co}$ =1495^{o}C) mechanical stirring was applied in order to obtain a homogeheous melt.

The alloy was cast in a cylindrical steel die having a diameter equal to 18mm. The alloy bar was considered to have been slowly cooled and its microstructure to represent the equilibrium structure. Further on samples cut from the cylindrical bar have been subject to rapid solidification.

Table 2

Chemical composition of the investigated Al-Co alloy (in wt.%Co)

Z	12	**13**	14	15	16	20	22
Symbol	Mg	**Al**	Si	P	S	Ca	Ti
wt.%	<0.01	**83.46**	0.4599	0.00359	0.00196	0.00152	<0.0002
Abs.error %	(0.0)	**0.05**	0.002	0.00009	0.00001	0.00004	(0.0)
Z	23	24	25	26	**27**	28	29
Symbol	V	Cr	Mn	Fe	**Co**	Ni	Cu
wt.%	<0.0001	<0.0001	<0.0001	0.175	**15.82**	0.04076	0.00443
Abs.error %	(0.0)	(0.0)	(0.0)	0.0007	**0.01**	0.00078	0.00014
Z	30	33	34	40	41	42	47
Symbol	Zn	As	Se	Zr	Nb	Mo	Ag
wt.%	0.01781	<0.00005	<0.00005	0.00075	<0.0001	0.00043	<0.0002
Abs.error %	0.00015	(0.0)	(0.0)	0.00008	(0.0)	0.00006	(0.0)
Z	48	50	51	52	72	73	74
Symbol	Cd	Sn	Sb	Te	Hf	Ta	W
wt.%	<0.0001	0.00083	<0.0003	<0.0003	0.00254	0.00257	0.00161
Abs.error %	0.00012	0.00015	(0.0)	(0.0)	0.00085	0.00011	0.00024
Z	81	82	83				
Symbol	Tl	Pb	Bi				
wt.%	0.00161	0.00213	<0.0001				
Abs.error %	0.00005	0.00006	(0.0)				

The rapid solidification has been carried out in a melt spinning apparatus (Fig.1) comprising a Cu roller 200 mm in diameter rotating at 2850 rot/min, resulting in a peripheric speed 29.82 m/s. The alloy in the quartz crucible was purged with argon and quickly melt by means of a high frequency induction coil.

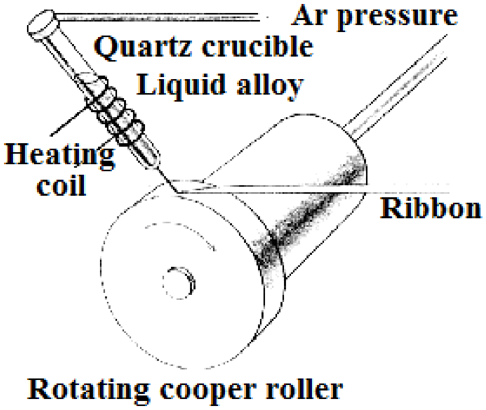

Fig.1. Schematic representation of rapid solidification by means of the melt spinning technique

After melting, an argon overpressure of 0.6 atm. was applied in order to expel the molten alloy through a 0.7 mm diameter nozzle bored at the bottom of the crucible. The distance between the nozzle and the surface of the rotating copper roller was small enough (0.5 mm) in order to maintain the hydrodynamic stability of the liquid metallic jet expelled through the nozzle. When in contact with the rotating copper roller, the metallic jet was splat as a thin ribbon that solidified at an extremely high cooling rate due to its extremely small thickness (less than 50 μm) as well as to the high mass of the copper roller that acted as a huge heat sink. The solid thin ribbon was continuously "spun" from the liquid alloy in the crucible and it detached itself from the copper roller surface due to centrifugal forces and contraction upon solidification. A 14 degree deviation angle from the vertical position of the crucible improved the conditions for continuous spinning of the thin solid ribbon. In the above mentioned conditions thin ribbons 2 mm wide and ~20 μm thick have been obtained.

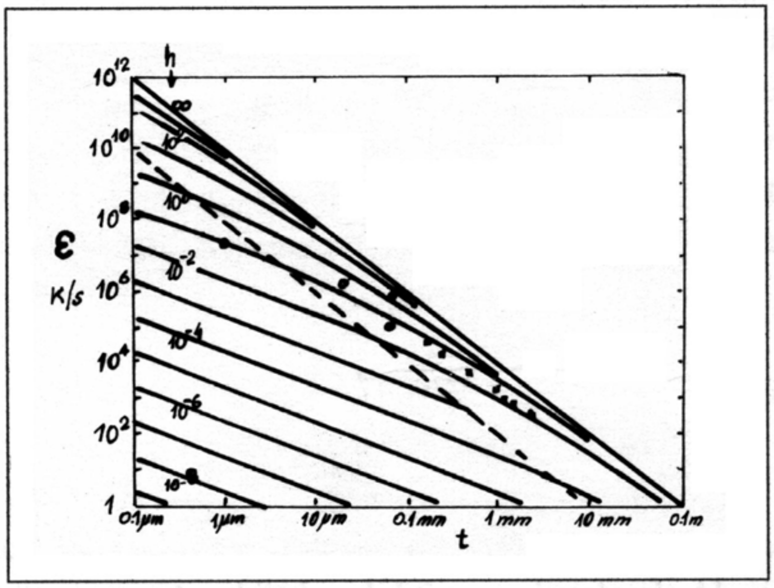

Fig.2. Correlation between the cooling rate ε during the solidification of Al in contact with a solid Cu heat sink and the thickness t of the solidified thin ribbon: ─── theoretic lines calculated for various values of the interfacial heat transfer coefficient (in W/mm^2,K); ● and ■ = experimental points

Concerning the cooling rate dT/dt (=ε) during the solidification of the melt spun ribbon, it cannot be measured directly. Instead it can be estimated from the thickness t of the ribbon that at its turn is dependent of the rotation speed of the copper roller, according to the following relationship:

$$dT/dt = \Delta T \kappa / ty \qquad (1)$$

where ΔT is the temperature difference between the melt and the copper roller, κ is the thermal diffusivity of the alloy on the highly conductive copper substrate, t is the thickness of the ribbon and y is a dimensionless variable with a typical magnitude of~3. By considering the values $\Delta T \sim 1000^oC$ and $t \sim 20\ \mu m$ in our experiment and a value $\kappa = 0.3\ cm^2\ s^{-1}$ reported in [4] for a melt spun Al-50wt%Ni alloy, we have estimated the cooling rate in our experiment to be $\sim 5x10^6\ ^oC/s$. This value is in good agreement the value estimated from the graphical dependence between ε and t in fig.2 proposed by Jones [5] by admitting a value $h = 10^{-2}\ W/mm^2,K$ for the interfacial heat transfer coefficient at the interface between the copper roller and the solidifying alloy ribbon. Concerning the cooling rate of the die cast bar it was approximated to be $\sim 5\ ^oC/s$ as specified in [6] for complex aluminium alloys. So, one may say that the melt spun ribbons have been cooled during solidification about one million times faster than the die cast bar.

3. Results and Discussion

Rapid soilidification is known to produce important phase and structural modifications in alloys, including (i) grain size refinement, (ii) solid state solubility extension, (iii) formation of new non-equilibrium intermetallic compounds, (iv) suppression of crystallization in favor of glass transition (amorfisation) during solidification.

The first effect may be put in evidence by electron microscope examination, while the last three ones by X-ray diffraction investigation. Hence both slowly cooled samples as well as rapidly solidified ones have been characterized by X-ray diffraction and by scanning electron microscopy.

The X-ray diffraction patterns in Fig.2 and Fig.3 have been recorded with $Cu_{K\alpha}$ radiation and further interpreted by using the ICDD-PDF-2 Release 2006 data bank. A software DIFFRAC plus Eva 12 (from the Brukker Comp.) was used both for obtaining the X-ray diffraction patterns from the “intensity versus theta angle” recorded listings as well as for searching in the data bank.

As seen in Fig.2 and Fig.3 the investigated alloy is polycrystalline in both conditions. Rapid solidification has not induced amorfisation and this was to be expected because the composition of the investigated aluminum-based alloy was not amorphisable. Indeed it was established since long time [7,8] that an Al-TM alloy (TM= a transition metal) becomes amorphisable only when large amounts of lanthanides (RE=rare earth) are added in its composition.

As seen in Fig.3 and Fig.4 the crystalline phases existing in the investigated alloy in both cooling conditions are the equilibrium phases fcc- Al and monoclinic-Al_9Co_2. The latter has been identified according to the ICDD-PDF number 3-65-6460 diffraction card in the powder diffraction file (PDF).

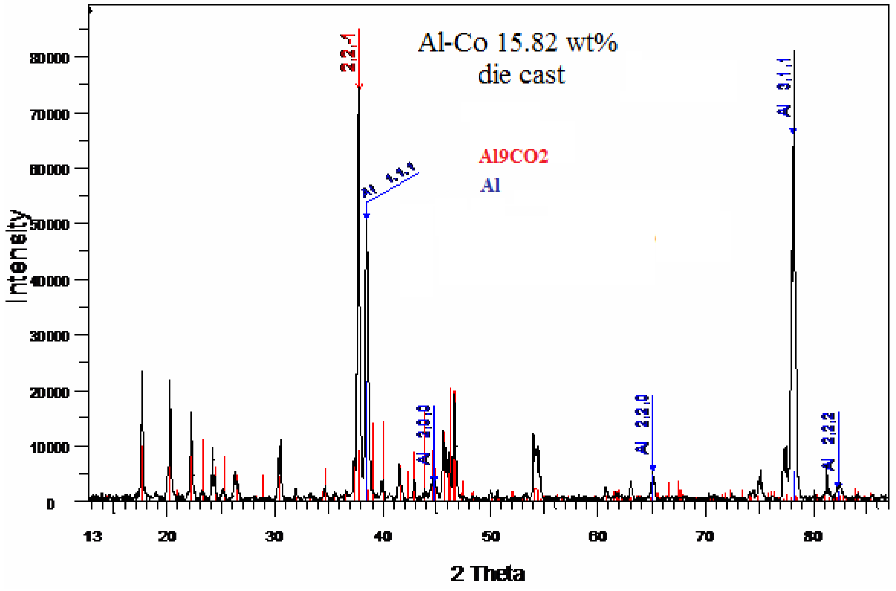

Fig.3. X-ray diffraction pattern of the die cast Al-15.82wt.% Co alloy with superimposed diffraction lines for fcc Al (in blue) and for the monoclinic Al_9Co_2 aluminide (in red)

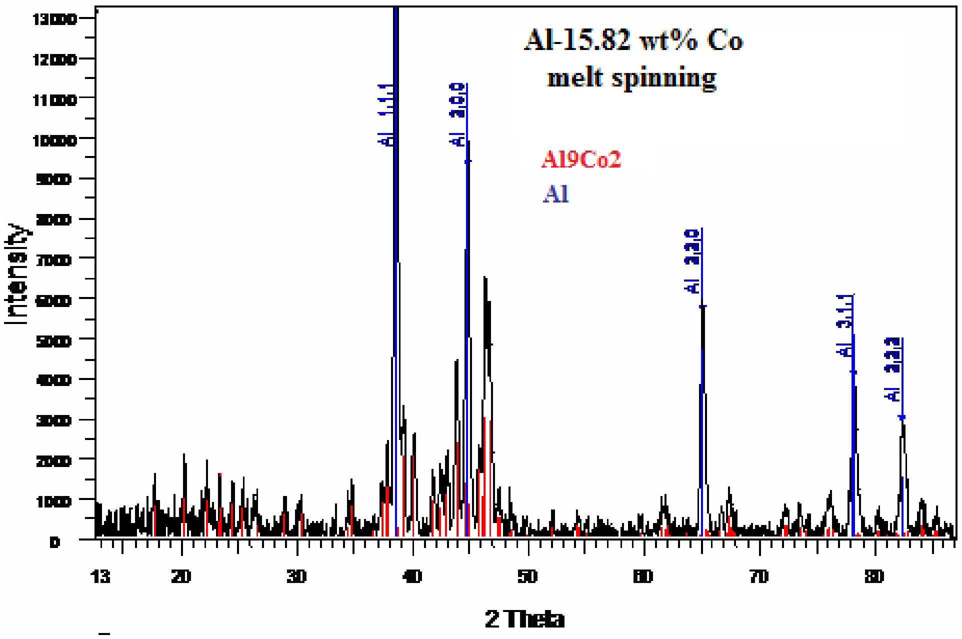

Fig.4. X-ray diffraction pattern of the melt spun rapidly solidified Al-15.82wt.%Co alloy with superimposed diffraction lines for fcc Al (in blue) and for the monoclinic Al_9Co_2 aluminide (in red)

So no metastable phases have been produced by rapid solidification, though in other Al-TM systems such metastable phases may appear, as for instance the Al_6Fe compound reported in continuously cast Al-2wt%Fe alloy [9].

The diffraction lines in the X-ray diffraction patterns in Fig.3 and Fig.4 show significant deviations from the intensity indicated in the corresponding cards of the powder diffraction file (PDF). This fact can be ascribed to a preferred orientation of the crystalline grains for both existing phases. This texture phenomenon is more clearly expressed in the die cast alloy and is less manifest in the rapidly solidified melt spun alloy.

The scanning electron micrographs in Fig.5 and Fig.6 clearly put in evidence the dendritic morphology of the Al_9Co_2 aluminide compound in the hypereutectic Al-15.82wt.%Co alloy in both solidification conditions (either rapidly solidified by melt spinning or relatively slowly solidified by die casting). As indicated in Table 2 there is a large difference in atomic number between aluminium and cobalt (Z_{Al} =13; Z_{Co} =27). On this account the presence of Co makes the Al_9Co_2 dendrites to look very bright and clearly distinct in the SEM micrographs in Fig.5 and Fig.6. The eutectic mixture of crystals ($Al+Al_9Co_2$) located in the interdendritic space is clearly visible in the SEM micrograph in Fig.5 for the slowly cooled alloy. This eutectic mixture seems to have a globular morphology of the dispersed phase (bright Al_9Co_2) embedded in the Al matrix (dark).

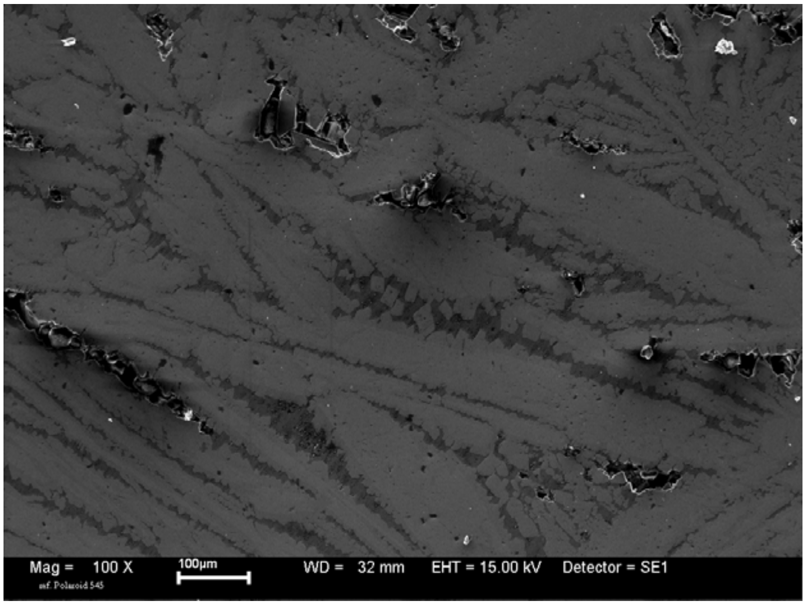

Fig. 5. SEM Micrograph of the die cast Al-15.82wt.%Co (composition image:atomic number contrast)

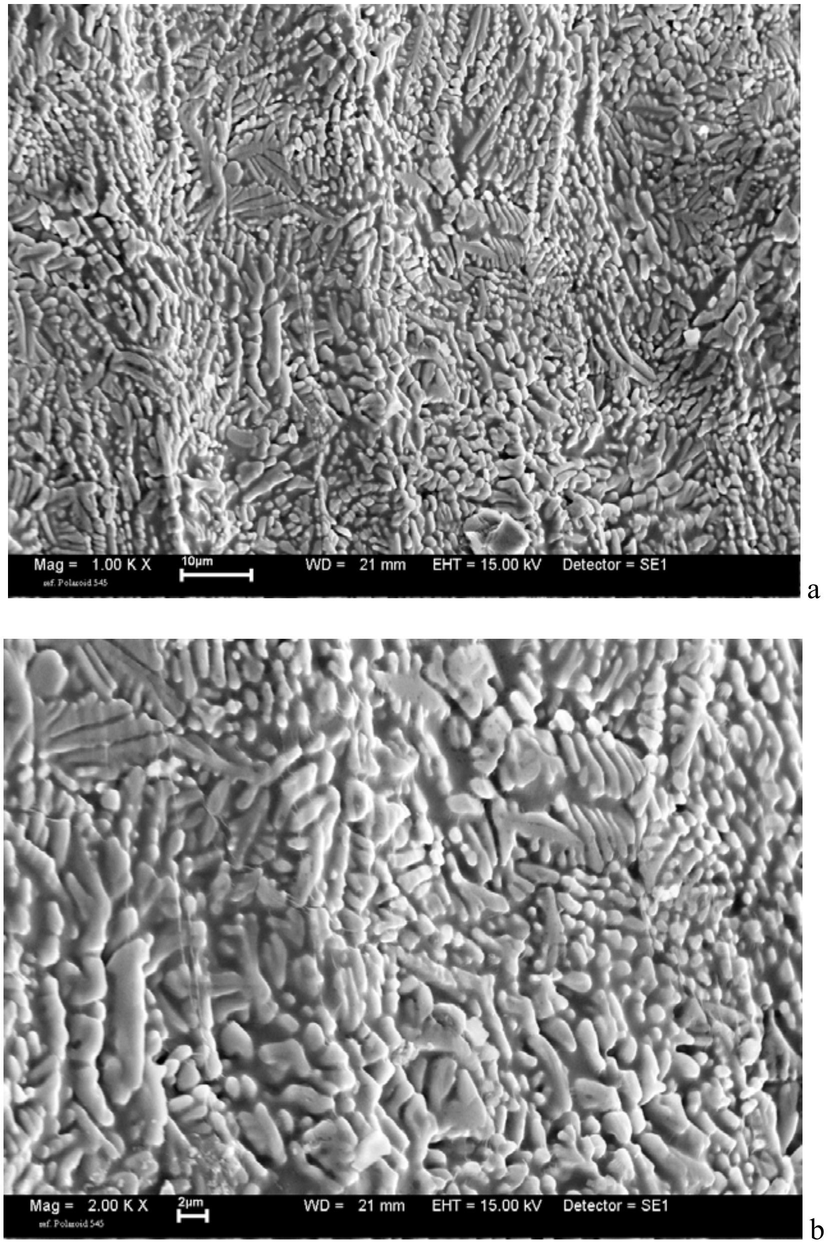

Fig. 6. SEM micrographs (composition image:atomic number contrast) of rapidly solidified Al-15.82wt.%Co; - micrograph **b** recorded at a higher magnification than micrograph **a**-

Ascertaining the dendrite morphology of the primary Al_9Co_2 compound in a hypereutectic Al-Co alloy is of both fundamental and practical interest. Indeed if such an alloy is intended to be used for making skeletal catalysts the dendrite morphology of the aluminide compound is of prime concern for ensuring the high specific area of the spongy metallic catalyst obtained by alkali leaching [10].

On the other hand, from a fundamental point of view, the type of morphology of primary intermetallic compounds, especially in less common alloys, has to be ascertained by experimental observation. Indeed the crystals grown in a supercooled melt may adopt either a faceted (idiomorphous) shape or a dendritic (alotriomorphous) shape depending on the value of the entropy change ΔS_m during the reversible melting/solidification process ($\Delta S_m = L/T_m$, where L is the latent heat of melting and T_m is the melting temperature).

Table 3

Values for the entropy at melting ΔS_m for various groups of chemical substances (cal/^{o}C,gram.atom)

Metals							Semimetal and Semiconductors					Most Inorganic substances
Alkaline	Terrous alkaline	Transition metals	Rare earth	Cu	Zn	Pb	Si	Ge	Sb	Bi	Te	
1.58-1.72	1.75-2.3	<2.3	1.08-1.58	2.0	2.3	2.2	7.18	6.36	5.19	4.77	5.8	>3.5

As seen in Table 3 the entropy at melting ΔS_m is small for metals and this is why the growing crystals adopt a dendritic morphology. In contrast to this semimetallic elements (including semiconductors) and most inorganic compounds have a large entropy at melting and as a consequence the growing crystals are idiomorphous being delineated by crystallographic faces. As far as the intermetallic compounds are concerned (as for instance the various aluminides in Table 1) depending on the aliquot of the metallic bonding in the mixed interatomic bonding, their entropy at melting may be either small or large, and consequently they may grow either as dendrites or as idiomorphous crystals.

What is really important for the aim of this paper is the impressive grain refinement for the primary Al_9Co_2 dendritic crystals brought about by rapid solidification. Indeed the SEM micrographs in Fig.5 and Fig.6 point to an enormous decrease in size for the Al_9Co_2 dendrites when the slow cooling rate during solidification was replaced by rapid solidification. Taking into account the magnification of each SEM micrograph in Fig.5 and Fig.6 the thickness of the stem of the Al_9Co_2 dendrites in the rapidly solidified alloy seems to be ~0.5μm, while in the slowly cooled alloy it appears to be ~100 μm. Hence replacing usual die casting by melt spinning seems to have produced a decrease in size for the Al_9Co_2 dendrites in the Al-15.82wt.%Co alloy estimated to be about 200 times if the thickness of the stem of the Al_9Co_2 dendrites was considered.

These preliminary results encourage us to continue the research by investigating the dendrite refinement by more precise measurements of the spacing between the secondary arms of the dendrites performed by image analysis and to investigate more thoroughly the influence of the cooling rate at intermediate values.

4. Conclusions

X-ray diffraction has ascertained the existence of the equilibrium crystalline phases fcc- Al and monoclinic-Al_9O_2 in the hypereutectic alloy Al+9.71at.%Co (15.82wt.%Co) both in die cast condition as well as in melt spun condition. So one may say that rapid solidification has not induced neither amorfisation nor formation of metastable phases in this Al-TM alloy.

SEM electron microscopy has indicated a dendritic morphology for the primary Al_9Co_2 crystals in both casting conditions that may be associated with a presumed low value of the entropy at melting for the Al_9Co_2 compound. The eutectic mixture ($Al+Al_9Co_2$) located in the interdendritic space seemed to have a globular morphology.

Concerning the grain size refinement induced by rapid solidification it was estimated to be ~200 times from consideration of the average thickness of the dendrite stems that was ~100 μm at slow cooling rate and ~0.5μm at rapid cooling rate.

More precise measurements by DAS (secondary dendrite arm spacing) would be useful for recommending Al-Co alloys in the investigated composition range as possible candidates for making skeletal catalysts. Such investigations are in progress for various intermediate cooling rates and for different compositions in the same range in the Al-Co system.

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