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METHOD AND INSTALLATION FOR OBTAINING METASTABLE STRUCTURES OF ALUMINUM ALLOYS

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Abstract: *It presents a new technology and device for rapid quenching of melt in order to produce ribbons with metastable structures. The method advantages are presented. It is estimated, based on obtained structures that the amount of cooling rate achieved with this installation is 10^5-10^6 °C/s. Obtained metastable structures of hypo-eutectic, eutectic and hyper-eutectic Al-Si and Al-Cu alloys are analyzed.*

Key words: *Al alloy, metastable structure, rapid quenching, microhardness.*

1. Introduction

It is known the properties of metal product depend on their structure. In order to obtain products with special or superior mechanical properties the routing structure assumes a fine-grained. This process is achieved by metallurgical and physical methods. The structure improving by means of metallurgical methods involves the treating of melt with chemical elements which significantly influence the germination mechanisms and/or growth of crystals. Physical methods refer to heat treatments of melt (overheating, stabilizing) which in first step leads to modification of melt structure. Other physical methods are applied during the solidification process (high cooling rate, vibration) and acts on the germination conditions and growth of crystals.

The most significant results were obtained by increasing the cooling rate during solidification.

A series of structural changes occur at solidification of an alloy when increase the cooling rate. These changes are presented below in order of increasing cooling rate: decrease of dendrites size and of their internal structures; emphasis of chemical homogeneity with reducing segregation; extension of solid solubility with formation of supersaturated solid solutions; occurrence of new metastable crystalline phases; formation of amorphous materials (metallic glass).

It appears that by increasing the cooling rate the quantitative changes of structure will lead to qualitative changes.

Under the influence of cooling rate, the fine-grained structure is estimated by the distance between the dendrites branches, called dendritic parameter. This inter-dependence is described by the following equation:

$$d = A \cdot v^{-n}, \tag{1}$$

where: d - dendritic parameter [μm]; v - cooling rate [°C/s]; A, n - constant.

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Variation of dendritic parameter is presented in Table 1, according to the amount of cooling rate for various processing technologies [5].

Table 1

Cooling rate and dendritic parameter for aluminium base alloys solidified by different processing technologies

Cooling rate [°C/s]	**Dendritic parameter [µm]**	**Processing conditions**
10^{-3}	1000	Sand casting parts Large diameter ingot casting in mould
10^{0}	100	Mould casting Continuous casting
10^{3}	10	Large granules
10^{6}	1	Small granules or flakes
10^{9}	0.1	Ultrafine flakes
10^{12}	0.01	Ultrafine flakes with initial large undercooling

In some works it considers that in case of wrought aluminium alloys the dendritic parameter variation depending on the nature and concentration of alloying elements is insignificant [2]. Therefore the curve of function (1) charted in double logarithmic coordinates can be used to determinate the cooling rate of any aluminium alloy processed with different cooling conditions.

In Table 2 are presented the "*n*" constant values from equation (1) for different aluminium alloys, based on data from literature [5].

The desire of increased cooling rate led inevitably to lower dimensions of the products obtained in form of powder or very thin ribbons, Figure 1 [1].

It is known that the intensification of cooling rate increases the undercooling degree which eventually determinate a finished structure by increasing the germination nuclei. This interdependence is shown in Figure 2.

Mentionable that the advanced finishing structure obtained by increasing the cooling rate requires both the changing of solidification techniques, and the technologies that provide the subsequent processing of the obtained solid material (isostatic pressing, brazing etc.).

Table 2

The "n" constant for aluminium base alloys (*after different authors*)

Alloy	**Cooling rate [°C/s]**	**n**
duralumin	0.007...2000	0.38
Al + (4.0...5.0)% Cu	<350	0.39
Al + Cu, Mg, Zn, Si	-	0.337
Al + (5.05...3)% Cu	<3	0.276
Al + (1.0...10.6)% Cu	0.67...5.0	0.25
Al + (5.5..26.6)% Cu	0.16...1.6	0.25
Al + (1.4...4.3)% Si	0.67...5.000	0.25
Al + (2.0....5.0)% Mn	10^{-10}...6.10^{-3}	0.32
Al + Cu, Si, Pd, Fe	10^{8}...10^{9}	0.33
Al + Mg	0.01...5.10^{3}	0.32
Al + Cu	0.01...5.10^{3}	0.37
Al + Fe	0.01...5.10^{3}	0.33
Al + Mn	0.01...5.10^{3}	0.377

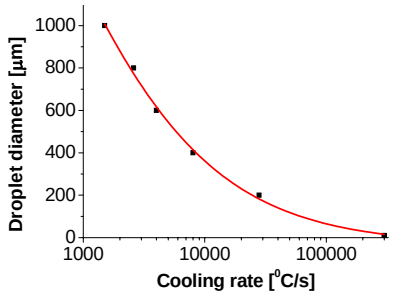

Fig. 1. *Interdependence: Cooling rate vs. particle dimensions*

Extension of solid solubility with the formation of supersaturated solid solution is presented in Figure 3.

In Table 3 are presented data on the extension of solubility of various chemical elements in Al solid state [2].

The intensification of cooling rate besides the formation of supersaturated solutions (metastable phases) can cause the appearance of new metastable crystalline phases.

Extension of solid solubility in Al Table 3

Alloying element	**Si**	**Mg**	**Cu**	**Ni**	**Fe**	**Ti**	**Mn**
Solubility equilibrium [% at]	1.6	18.9	2.8	0.023	0.025	0.15	0.7
Extended solubility [% at]	10-16	36.8-40	31-30	5.2	6	2	9

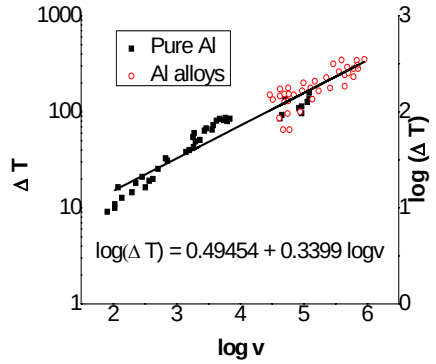

Fig. 2. *Variation of undercooling degree for Al and Al-based alloys depending on the cooling rate*

At specific categories of alloys (compositions) this technological version for improving the structure has led, besides quantitative changes in the structure, to the occurrence of new types of materials with nano and amorphous structure characterized by exceptional mechanical and physical properties.

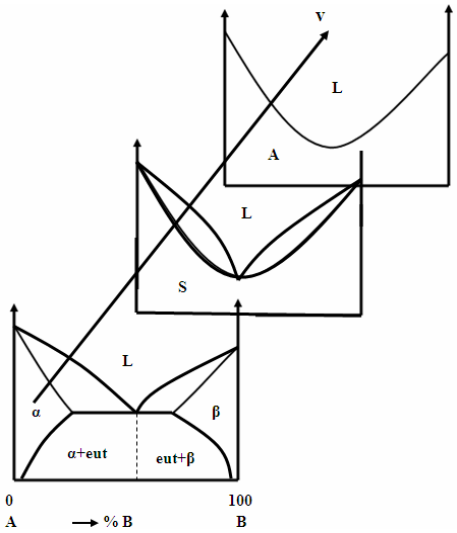

Fig. 3. *Extension of solubility at high cooling rate* (*L - liquid, S - solid, A - amorphous*)

Since the discovery of metallic materials with an amorphous structure (Pol Duwez-1960), researches carried out with great intensity to discover new types of alloys with metastable structures that have particular mechanical, physical and chemical properties.The importance of studying the structure of metallic materials with metastable structures also highlights the topic of international conferences: „International Conference on Rapidly Quenched and Metastable Materials" has reached its 14th edition and „International Symposium on Metastable, Amorphous and Nanostructured Materials" is at 17th edition.

The current technologies for processing thin ribbons, with tens of microns thicknesses, by rapid expulsion of liquid metal on the rotating disk surface (melt-spinning method) does not allow the change of expulsion speed in wide enough limits and at the same time is not possible to overheat or melt thermal treatment.

2. Experimental Plant

In order to achieve increased cooling rates applied to the melt, in the processing laboratory of nonferrous alloys was tested a device designed to producing metal ribbons.

The experimental device combines the cooling technology of metal jet on rotating disk of copper or steel with the fuel system of the rotating disk of liquid alloy with the principle of low pressure casting technique, Figure 4. This device is the upgrade version of the one presented in [3], [4].

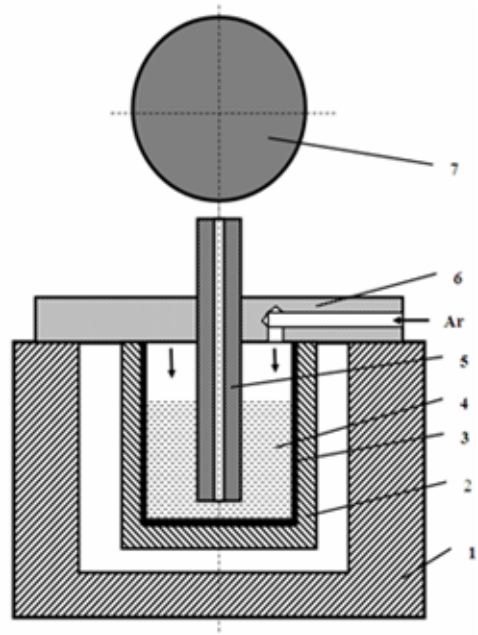

Fig. 4. *Experimental device for producing ultra-rapidly cooled thin ribbons*
1 - furnace; 2 - support of crucible; 3 - graphite crucible; 4 - liquid alloy; 5 - connecting part; 6 - sealing cap; 7 - spinning disk

At low pressure casting technology the transport of liquid alloy from the furnace to the cavity form, located above the oven, is ensured by creating an overpressure on the free surface of the melt. This approach assumes that the crucible with liquid metal to be placed in a sealed space. Thus the melt is forced to move vertically through the connecting tube.

In case of the plant from Figure 4, the working gas (Ar) introduced by the channel practiced in the sealing cap (6) acting on the liquid alloy (4) from the crucible (3) causing the lifting of melt in connecting part (5) and its expulsion on the rotating disk (7).

The speed and flow of the melt at the top of the feeding tube is adjusted both by the appropriate choice of flow and pressure at the working gas as by the interior diameter of feeding part. These factors will determinate the ribbons thickness.

3. Experimental Determination

In the experimental determinations have been processed a series of aluminium based alloys which present technical importance: eutectic, hypo- and hypereutectic alloys from Al-Si system, monophasic and biphasic alloys from Al-Cu system and monophasic alloys from Al-Mg system.

In order to identify the structural changes in case of liquid quenching in parallel with the processing of alloys by melt-spinning technique, samples were cast in steel mould with 160x80x14 mm dimensions.

The semi-products obtained by these casting technologies have been subjected to both heat treatments of annealing and solid quenching.

In this stage, structural changes were determinate by optical microscope and by determining the microhardness.

The amount of cooling rate was determined by processing a hypereutectic Al-Si alloy with composition [wt.%]: Si - 23.97; Mg - 0.06; Mn - 0.04; Fe - 0.7; Cu - 0.21; Cr - 0.012; Zn - 0.1; Ni - 0.08; Ti - 0.05; Pb - 0.026; Sn - 0.003. The size of primary silicon separations from the obtained ribbons were less than 1 μm, Figure 5 (ribbon thickness is 100 μm).

Fig. 5. *Experimental installation and the obtained ribbon*

Based on the relation (2), [2]:

$$\lg[d] = -0.354 \cdot \lg[v] + 2.013, \qquad (2)$$

it can be concluded that the value of cooling rate situated in the 10^5-10^6 °C/s limits.

In case of Al-Cu alloys the obtained structures are shown in Figures 6 and 7.

The microstructure analysis of Al - Cu10 ribbon confirms the value of 10^5 - 10^6 °C/s for the cooling rate.

The microhardness obtained for the two compositions are presented in Table 4. The values listed in this table represent the average of at least 10 measurements.

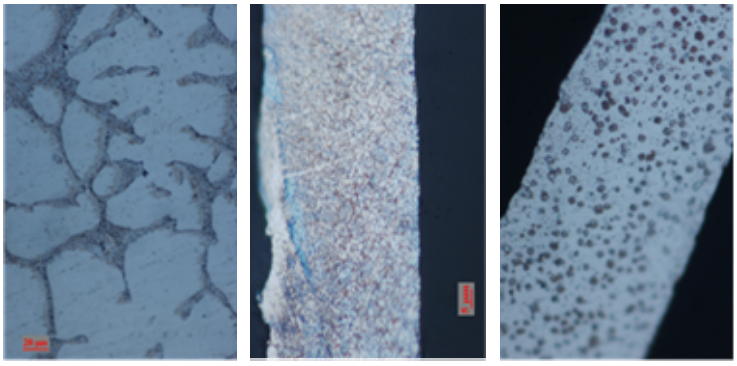

Fig. 6. *Structures of Al - Cu10 alloy: a) cast in steel mould; b) ribbon obtained by melt-spinning technique; c) ribbon from b) point after annealing (t = 500 ^{0}C, τ = 2 h), x1000*

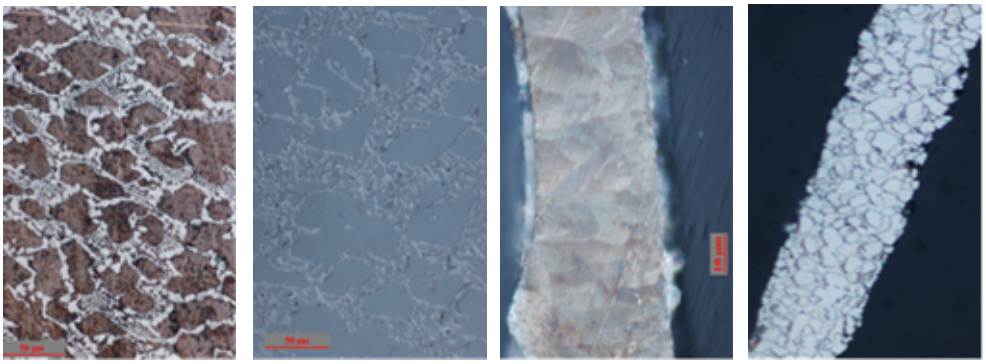

Fig. 7. *Structures of Al-Cu35 alloy: a) cast in steel mould; b) alloy from a) point after annealing (t = 500 ^{0}C, τ = 2 h); c) ribbon obtained by melt-spinning technique; d) ribbon from c) point after annealing (t = 500 ^{0}C, τ = 2 h), x1000*

Microhardness of processed alloys HV 0.01 Table 4

Alloy	**Al-Cu10**		**Al-Cu35**	
Material conditions	**Casting**	**Annealing**	**Casting**	**Annealing**
Gravity cast in steel mould	83 - for s.s.α	60 - for s.s.α	240	177
Processed by melt-spinning technique	116	49	346	163

4. Conclusions

The processing variant of liquid alloy described submits at least three advantages compared to conventional technologies, namely: allows overheating of the melt in much higher limits; the shape and size of the hole through which expels the liquid alloy can be modified in much larger range; the supply version of the disk rotating with tube immersed in liquid alloy provides extraction of a less contaminated melt with metallic and non-metallic solid inclusions.

It should be noted that feeding variant of spinning disk with liquid alloy is much simplest and easier to adjust that the version with the supplying of melt above the rotating disk.

However, the version presented allows an increasing of high cooling rates effects required by the structural characteristics of processed ribbons.

The installation enables the study of structural heredity process which is manifested by the relationship between metal-charge, melt and cast product.

The materials obtained by this technology can still be used for structures modification (fine-grain) of cast alloys as parts or semi-products.

Formation of metastable phases and supersaturated solid solutions were confirmed by the hardness values obtained for the ribbons processed by melt-spinning method.

Decomposition study of metastable structures achieved by presented installation, by DSC and dilatometer analysis, X-ray diffraction and electronic microscopy will make possible the obtaining of new information about thermodynamics and kinetics of these transformations.

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