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Manufacturing of cellular A2011 alloy from semi-solid state

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Materials

ABSTRACT

Purpose: The work presents a new method to produce cellular metallic material by pressing the alloy in the thixotropic semi-solid state into a layer of space holder particles, which are removed from the product after the forming operation.

Design/methodology/approach: It is investigated the influence of the thixoforming temperature and the size of space holder particles, in the ability of penetration of the slurry in the porous pre-form as well as the structure of the obtained porous material (general aspect, quantitative and qualitative characterization of porosity, microstructure of cells walls and density of the product).

Findings: Cylindrical samples presenting three different ranges of porosity were produced. The cellular material obtained contains open porosity, being characterized as sponge. Products were analyzed by tomography and metallographic techniques. Results show that the proposed process is able to produce acceptable porous material, in a simple and low cost technique. The quality of the product depends rather on the processing temperature than on the size of space holder particles. Low liquid fraction in the thixotropic slurry can lead to incomplete infiltration and deformation of the pre-form. In the analyzed conditions influence of the size of space holder particles could be observed neither in the processing ability nor in the quality of the product. Density of produced porous material increases as processing temperature increases, due to the increase of cells walls thickness.

Research limitations/implications: The investigated process is suitable only for alloys with a significant solidification range.

Practical implications: Tthe new method to produce cellular metals can represent energy savings and is highly operational when compared to conventional methods based on liquid infiltration, since lower temperatures are involved and no need of liquid handling is required.

Originality/value: the process proposed is a new one; no techniques based on thixoforming of the alloy into porous pre-forms are known so far.

Keywords: Mettalic alloys; Cellular material; Porous material; Metallic foams; Metallic sponges; Thixoforming

1. Introduction

Cellular materials, particularly metallic foams and sponges have been increasingly used in commercial applications in the last decades, merging as a new class of engineering materials, due to their particular and interesting combination of properties: low specific weight, high stiffness, good energy absorption in impact, thermal and acoustic insulation, vibration damping, among others [1, 2]. Some examples of commercial application of metallic foams and sponges based on Al alloys can be found in the automotive industry, as foams sandwich panels, structural parts, components, impact absorbers [3]. Although most of the developments and commercial application of metallic cellular material are related to Al alloys, other metals or alloys like iron, steels, titanium, lead, zinc, can also be produced in porous form for different purposes, as filters, membranes, biomedical applications, etc. [4].

Several manufacturing processes have been under development and are available for the production of cellular metals and alloys, which can be gathered in groups according to the state of the starting metal or precursor: liquid or solid (powder) [5]. Processes can involve foaming of the metal by gases which can be introduced in the liquid by external sources – direct blowing of inert gas; added blowing agents can be dissociated *in situ* generating gas in the liquid; dissolved gas can be forced to precipitate, etc. The foaming agent can be introduced in the liquid metal or, most commonly, a compact of the metal and the blowing agent powder is heated at temperatures above melting of the metal. In any case, foaming occurs in the liquid state.

Foams are highly unstable systems and the success of a foaming process depends on two basic factors: the appropriate entrapment of the gas element in the liquid and surfaces stabilization. Therefore, viscosity control of the liquid is critical as well as the presence of interface stabilizers like ceramic particles (SiC, Al_2O_3).

Difficulties in controlling the foaming parameters lead to the development of alternative routes to produce cellular metals. Among these the solidification of the metal in confined spaces among particles or nets of non-reagent material, which is removed after the processing, showed to be promising. The process requires the infiltration of liquid metal into porous pre-forms; by removing the so-called “space holders”, the product presents high porosity and is characterized as cellular material with open cells or sponges [6].

This work aims to contribute to the development of this exciting new class of materials by investigating the feasibility of producing porous metallic materials by infiltration of the metal in the thixotropic semi-solid state, into a porous layer of water-soluble space holders. Therefore, lower temperatures can be used when comparing to liquid infiltration processing, resulting in higher operationally and costs savings.

2. Experimental procedures

A2011 alloy was used in the experiments, with basic composition Al-5.3%Cu, 0.27%Si, 0.4%Fe (wt %).

As space holders NaCl particles were used. This material is stable in liquid Al in the processing conditions (temperatures and time) and can be easily removed from the product after infiltration and solidification. Particles with poliedric geometry and 3 distinct dimensions were used: fine particles (1.6mm > ϕ_F > 1.0 mm), medium particles (3.15mm > ϕ_M > 1.6mm) and coarse particles (ϕ_C > 3.15 mm).

As the alloy was processed in the semi-solid state, it was mandatory the previous knowledge of the *solidus* and *liquidus* temperatures, in order to properly define the thixoforming processing. DTA tests showed a solidification range between $T_{solidus}$ = 612 ± 2ºC e $T_{liquidus}$ = 638 ± 2ºC.

For thixoforming tests, sandwichs of two metallic disks with dimensions ϕ 44.5mm x h 10mm with an internal 20mm thick layer of space holder particles were posicioned in a steel die inserted in a furnace on a press table. Metallic disks were machinned from extruded bars.

All assembly was heated to temperatures within solidification range; after reaching the thixotropic condition, samples were forged. Tested temperatures varied from 620 to 640°C, necessary for the required partial melting and spheroidization of the structure; liquid fractions in the thixotropic slurry varied theoretically from 50 to 90%.

Figure 1 illustrates the experimental procedure. Temperatures in the metallic disks as well as applied forces were monitored during thixoforming operation.

After infiltration and total solidification of the alloy, particles of space holders were washed out in hot water, resulting in a porous product.

Products were characterized concerning density, porous architecture and microstructure of cells walls. For metallographic preparation porous samples were infiltrated with transparent resin to allow cutting and polishing without destroying cells walls. Keller’s etching was used for microstructure analysis.
Porous architecture was analyzed by tomography; images of parallel sections were taken each 1.0mm.

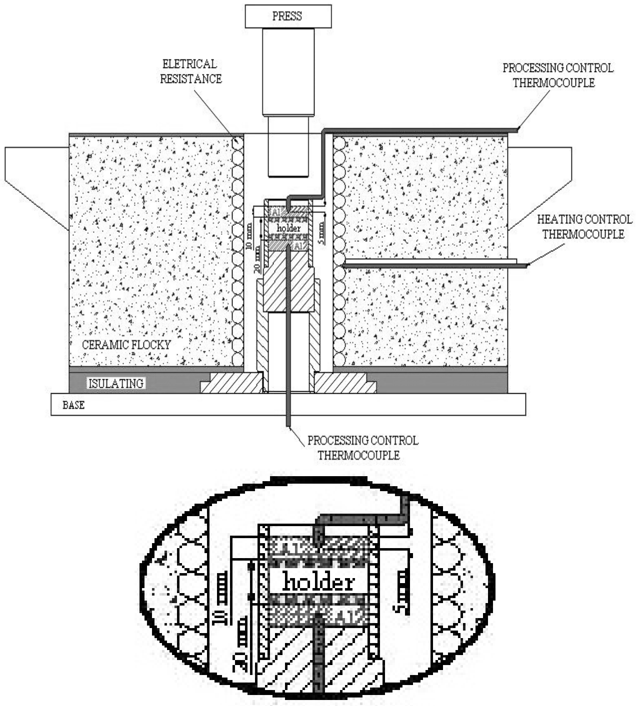

Fig. 1. Schematic representation of the infiltration process of semi-solid thixotropic A2011 into a layer of space holder particles, to produce porous metallic material

3. Results and discussions

3.1. General aspects of obtained products

It was possible to obtain reliable porous products in almost all conditions tested. No reaction of space holder particles with the alloy was noticed. Space holders were completely washed out of the porous material, since no entrapment of any particle was detected in the final product. Even without any previous sintering of space holder granules, there was sufficient contact among them to prevent their entrapment in the metal matrix. Leaching has to be made carefully in repeated operations, using ultra sound and cleansing in hot water repeatedly, to prevent retention of any salt particle.

Figure 2 shows typical samples obtained. It can be clearly observed that porous cavities are interconnected, which allowed the total removal of space holder particles, and characterizes the material as a sponge. The sizes of porous cavities present the same order of magnitude than the size of space holder particles utilized; coarse particles resulted in porosity with higher dimensions.

It can be also observed apparently good macroscopic dispersion and regularity of porosity. However, the remaining compact Al alloy layers encapsulating the porous region present different thickness for different processing conditions, revealing different penetration ability of the semi-solid during thixoforming operation.

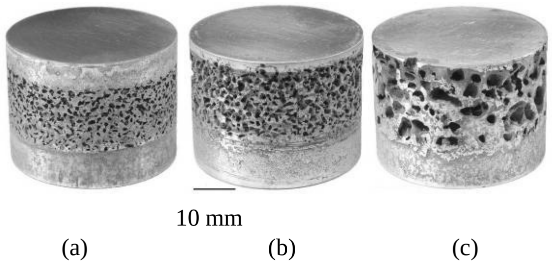

Fig. 2. General aspect of typical cellular A2011 alloy produced by thixoforming into a layer of space holder particles. a) and b) fine particles; c) coarse particles. Thixoforming conditions: (a) T = 620°C; (b) and (c) T=640°C

As forming temperature increases, liquid fraction in the thixotropic slurry also increases, improving the infiltration of the space holders layer, as it could be observed comparing samples produced at 620°C and 640°C.

In all conditions, the bottom layer of Al alloy was not infiltrated; temperature monitoring during processing shows that this region did not reached the desired temperature to promote sufficient liquid fraction in the alloy which was confirmed by microstructure observations (micrographies to be shown in section 3.3.

In cases where infiltration was poor, internal defects were observed by tomography analysis. Such situations occurred in some samples produced by forming the alloy at the lowest tested temperature (620°C), i.e. with the lower liquid fraction, associated with another critical condition: space holder particles with the finest dimensions. These conditions revealed to be critical, with no guarantee of repeatability of good results. In some cases, resulting product was too brittle to be handled, due to excessively thin metallic cells walls, as observed in Figure 3.

General results concerning infiltration ability according to processing parameters are presented in Figure 4. The ability of infiltration is evaluated indirectly accordingly to the resulting thickness of the layer of porous material. It is not shown results concerning the fine and medium space holder particles + lower temperature, once the products in these situations were too brittle due to thin cells walls, as mentioned earlier, or, in some cases, lack of metal infiltration.

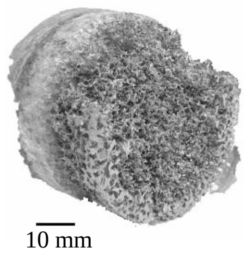

Fig. 3. General aspect of cellular A2011 alloy produced by thixoforming at T = 620°C into a layer of fine space holder particles

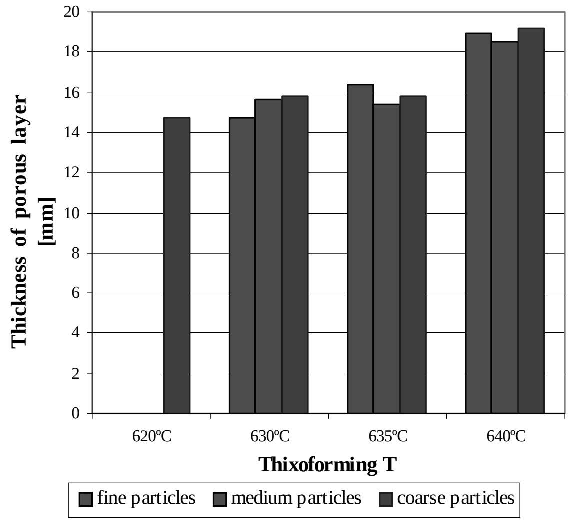

Fig. 4. Thickness of porous material x processing parameters - evaluation of infiltration ability of thixotropic A2011 into a layer of space holder particles with different dimensions

Results show clearly the influence of temperature, meaning liquid fraction in the metallic slurry: higher the liquid fraction, higher the infiltration ability. On the other hand, the influence of dimensions of space holder particles can not be established in situations where the liquid fraction is high. However, in cases where liquid fraction is low, the utilization of space holders with small dimensions can jeopardize the success of the processing.

Therefore, the proposed process is suitable to produce reliable porous material in a wide range of operational conditions; is easily operated and low cost – neither special apparatus is required nor laborious routes.

However, special attention must be paid when dealing with thixotropic material with low liquid fraction and fine space holder particles.

3.2. Architecture of porous

Cellular materials are characterized by the porous “architecture”, i.e. their volume fraction, dimensions and distribution, as well as thickness of cells walls. These are the structural parameters generally used to correlate structure x properties of a porous material.

As a general statement, as the material presents high percentage of its volume as voids, the metallic content - cell walls - represents low restriction to deformations, resulting in higher capacity of impact energy absorption and high plastic deformation.

Concerning the dimensions and geometry of porous, the majority of cellular materials is inherently heterogeneous, showing variations in the architecture of porous and mass distribution. These materials are usually formed by a three-dimensional net of the metallic matrix with variable cells walls thickness, containing usually 70 to 90% of empty space.

Samples of cellular A2011 produced by thixoforming were sectioned after infiltration with transparent resin to fill voids, to show the internal architecture. Some typical results are shown in Figure 5.

It is possible to observe that porosity is interconnected; geometry of porous is highly irregular, somewhat difficult to be characterized. The interconnection of voids, intrinsic characteristic of sponges, give the material some specific properties for application in situations where flowing of fluids through the porous is required, as for example in filters, heat exchanges and electrochemical cells.

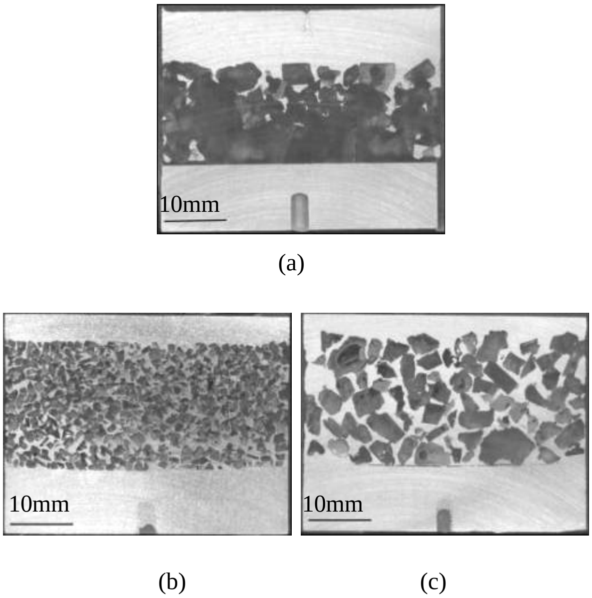

Fig. 5. Transversal sections of typical samples of cellular A2011 alloy produced by thixoforming in different conditions: (a) T = 620°C, coarse space holder particles; (b) T = 640°C, fine space holders particles; (c) T = 640°C, coarse space holder particles

Cells walls present thickness values varying from as small as 0.1mm to as big as 5.0mm. Measurements show that the coarser the space holder particles used coarser the thickness of cells walls, as expected. These values don't depend on the thixoforming temperature, indicating full infiltration of the semi-solid alloys in all the analyzed samples (except those produced under the critical conditions mentioned earlier).

In all cases it could be observed some cavities with dimensions smaller than the particles used, indicating the possibility of their fragmentation in the forming process; as well as cavities with dimensions bigger than the original salt granules as a result of their agglomeration. Indeed, it can be observed in Figure 5 (a) that particles can be compressed against the bottom metallic layer promoting the formation of a big cavity in this region, in the final product. This situation could be observed when low liquid fraction was present in the semi-solid alloy, making it difficult to flow within the layer of space holder granules. As thixoforming temperature increases, the possibility of compression of the salt layer decreases, as well as the presence of big voids in the cellular product. Moreover, the thickness of the layer of cellular material increases as observed previously in Figure 4.

All samples of cellular A2011 produced were submitted to X-Ray tomography for evaluation of the internal distribution of the porosity and the presence of defects related to lack of infiltration. Typical results are presented in Figure 6.

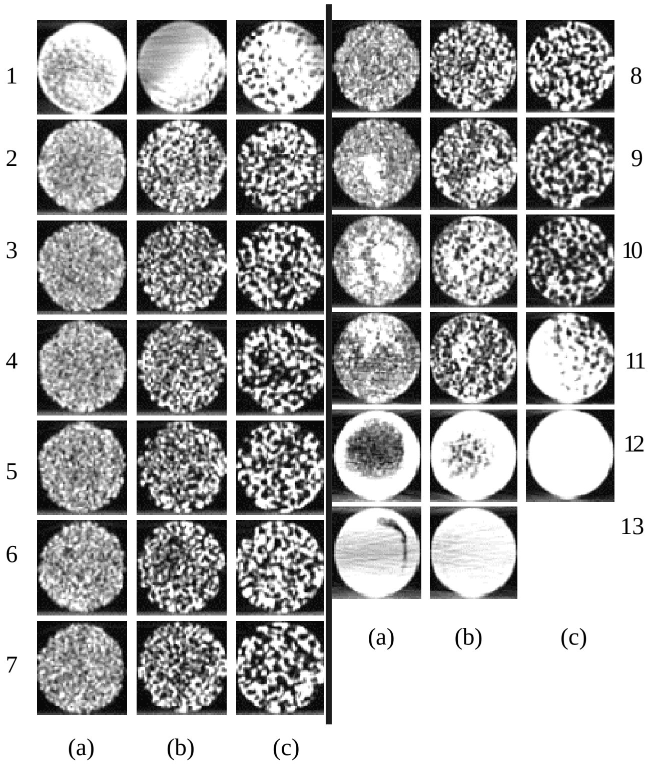

Fig. 6. Tomography images of cellular A2011 produced by thixoforming at 640°C, into a layer of space holder particles with dimensions: (a) fine; (b) medium; (c) coarse

Images shown correspond to parallel consecutive plans, from top (1) – upper metallic disk, to bottom (12) – bottom metallic disk, passing through the porous layer.

It can be observed for the condition presented in Figure 6 (high liquid content in the semi-solid alloy), good dispersion of porous and reliable products, independent on the size of particles used as space holders.

As a general result, it could be confirmed that the porous are interconnected in the samples obtained in all conditions analysed. The distribution of porous can be considered, in general, reasonably homogeneous in the whole volume of porous material produced, except in some cases where the processing parameters allowed agglomeration of particles, leading to incomplete formation of cell walls. The particular conditions where the incomplete filling of the porous layer resulted in unacceptable product were already discussed: low liquid fraction in the semi-solid alloy + fine dimensions of the particles of space holders. Results obtained in these conditions are shown in Figure 7. It can be observed a dark region in the center of the section, towards the bottom of the sample, indicating incomplete filling in this region.

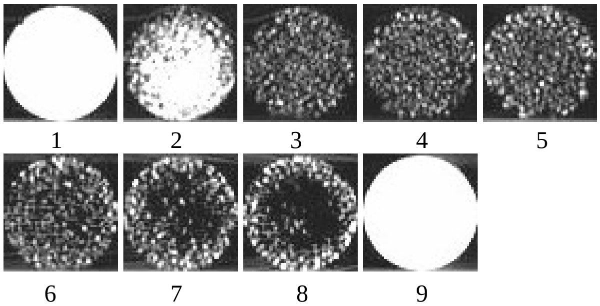

Fig. 7. Tomography images of cellular A2011 produced by thixoforming at 620°C, into a layer of fine particles of space holders. Sections from top (1) to bottom surfaces (9) of cylindrical samples

3.3. Microstructure of cells walls

During processing in the semi-solid state, the flow behavior of the metallic material depends on the constituents of the slurry, i.e. the liquid fraction/solid fraction ratio and on the characteristics of the solid phase: its morphology and dimensions. These features can be evaluated and determined by analysis of the microstructure of the solidified slurry.

As far as cellular materials are concerned, in spite the usual characterization of their mechanical properties related to the porous architecture, also the microstructure of the metallic component – cell walls – can exert significant influence in the materials performance.

Microstructure of metallic walls can present different phases with different growth morphology (dendritic, needle-shape, eutectics, etc.) and also brittle constituents, which can determine the metal mechanical behavior. In the particular case of cellular alloys produced by foaming, for example, it is necessary during processing the addition of surface stabilizers, being ceramic particles like SiC and Al_2O_3 the most commonly used [7]. The need of addition of such particles represents an extra difficulty to the processing, once their wetting, entrapment and dispersion in the liquid must be properly controlled. Processes other than foaming, as the proposed route, can be interesting alternatives to eliminate such difficulties.

In order to analyze both the microstructure of the semi-solid slurry before thixoforming and the final microstructure of the cellular material produced, all the samples obtained had their transversal section metallographically prepared.

Micrographies of three different regions of samples produced at different temperatures, using coarse space holder particles, are shown in Figure 8: top metallic disk, central porous layer and bottom metallic disk.

It can be observed that the structure of the upper metallic disk presents globular primary α phase surrounded by eutectic (α + $CuAl_2$) in all cases. Small globules of eutectic phase are present within the globular primary α. It can be considered that at least the eutectic phase observed in the solidified material was liquid in the semi-solid state.

These structures are typical of thixotropic slurries produced by partial melting. When heated to the solidification range, secondary phases with lower melting point originate liquid around the higher melting point primary phase. By holding the material at such high temperatures, morphology of primary phase turns to globular in order to decrease superficial energy, in a natural, thermodynamically commanded phenomenon. This morphology modification occurs through coarsening mechanisms involving mass diffusion, as described elsewhere [8] and can allow liquid entrapment in the modifying structure, resulting in the pools of eutectic phase observed within the primary globular phase.

Average diameter of solid globules in the thixotropic slurry is in the range 320 to 340μm, according to measurements. These dimensions can be considered high when dealing with thixotropic metals, but still the slurry is perfectly viable of flowing among the space holder granules used.

In spite of the extruded condition of the initial material, which could promote the formation of fine globular structure in the semi-solid state, heating time was long enough to allow the excessive grain growth observed. This aspect of the process must be improved to ameliorate flowing behavior of the thixotropic metal, its infiltration ability and as consequence, the product quality.

It can be observed in the photos the effect of increasing processing temperature: higher the temperature, higher the liquid content in the slurry to be infiltrated.

The microstructures of the metallic disks placed in the bottom part of the sandwich present significantly lower liquid fraction for all temperatures used. Indeed only slight amount of liquid could be observed in samples treated at temperatures lower than 640°C. This explains the lack of infiltration from the bottom disk metal; therefore, with appropriate heating control during processing it can be produced porous material with encapsulating metal layers of different thickness.

Analysis of microstructure in the central part of the products – porous region – allows the understanding of the flow behavior of the thixotropic metallic slurry in different processing temperatures. It can be observed in the sample produced at the lower temperature, i.e., lower liquid fraction in the thixotropic material, that the metallic cells walls present a rather distinct microstructure than the microstructure of the upper metallic layer (it was commented previously that no infiltration upwards from the bottom metallic disk was observed).

Cells walls microstructure presents fine α phase with dendritic morphology, a typical as-cast situation obtained from liquid solidification. This result shows that there was no

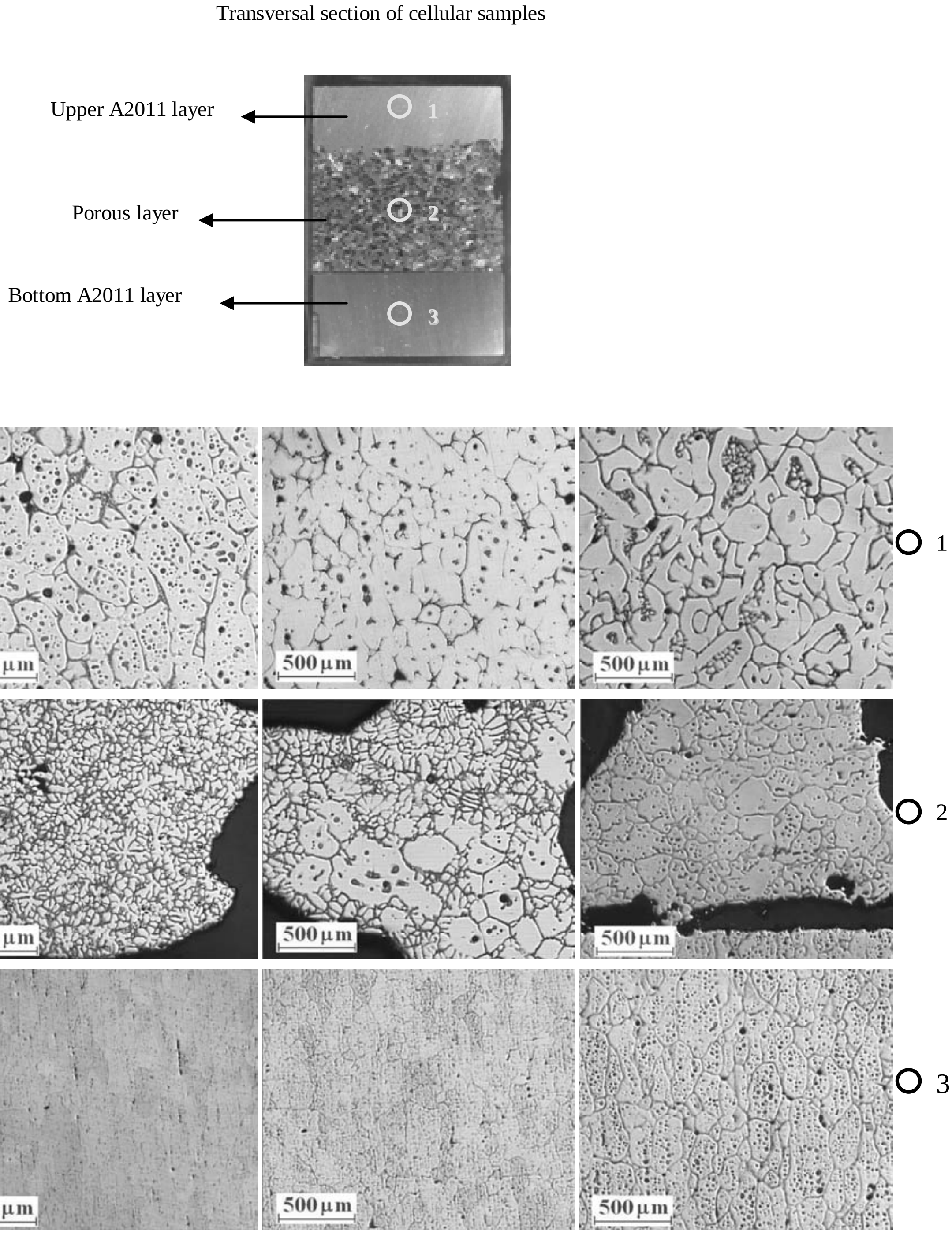

Fig. 8. Microstructures of cellular A2011 produced by thixoforming into a layer of space holder particles with coarse dimensions. Thixoforming temperatures: (a) T = 620ºC; (b) 630ºC; (c) 640ºC. Regions shown according to indication

infiltration of the slurry as a whole, but the liquid alone was pushed through the porous layer of NaCl granules. Segregation of liquid during thixoforming processing was already observed in forging operations [8] and can be reduced by increasing forming rate.

As forming temperature increases, microstructure of cells walls tends to be more similar to those of the thixotropic slurries from which they were formed, as shown in Figure 8 (b) and (c). It can be observed that microstructures produced by thixoforming at 630°C present α phase with morphologies both dendritic - resulted from conventional liquid solidification -, and globular, similar to that of the thixotropic slurry in the upper region. This result indicates less separation of solid and liquid phases during processing; the higher liquid content allowed the flowing of the slurry as a whole. Indeed, at the higher temperature – higher liquid content in the thixotropic slurry -, the microstructure of cells walls shows a typical thixocast structure, similar to that of the remaining compact metal layer at the top of the sample.

Thixocast structures as the observed in the porous material produced from slurries with high liquid fraction can present similar mechanical behavior as dendritic structures, in cases where free distances for displacement during deformation are of the same order of magnitude. As observed in previous work [10], if dendrite arm spacing of α phase in as-cast Al-Cu alloys structures is similar to globules diameter in thixocast structures of the same alloy, their mechanical properties (yield strength and total % elongation) are similar.

As observed in the results, however, coarse globular α phase is obtained.

Although mechanical tests were not yet performed at this point of the ongoing work, it is possible to suppose that the deformation behavior of the produced porous material is high, as far as the cell walls are concerned, which can be interesting for this kind of material. In addition, as neither any contamination of the metal by the space holder particles was observed, nor their entrapment in the porous material, nor hard particles from foam stabilizers are present in the produced structures, an appropriate mechanical performance of the cellular material can be predicted.

3.4. Density

In general a material is classified as cellular when presenting apparent density in the order of up to 30% of the apparent density of the bulk material. Technical literature [6] points out the possibility of obtention of sponges of Al and some of its alloys by liquid infiltration into space holders pre-form, with apparent densities around 10 a 50% of that of the compact material.

Results on density of cellular A2011 produced by thixoforming at different temperatures into a layer of space holder particles with different sizes are presented in Table 1.

It is not shown results of samples produced at 620°C using space holder particles of fine and medium sizes due to their excessive fragility as mentioned previously.

It can be observed for all conditions tested except one, a relative density of the cellular to the bulk material smaller than 0.30. The exceptional case was obtained for the highest temperature + coarsest granules of NaCl.

Concerning the influence of the processing variables temperature of the thixotropic alloy and space holder particles size, it can be observed a tendency of higher values of density with increasing processing temperature. This tendency can be attributed to the increase of cell walls thickness with increasing the infiltration ability of the semi-solid: the highest density was obtained in the cellular material produced from semi-solid with the highest liquid fraction infiltrated to the coarsest particles.

It was also evaluated the voids contents in the cellular material produced in all conditions tested. Results are shown in Figure9.

Table 1.
Density of cellular A2011 produced by thixoforming the alloy at different temperatures into a layer of space holder particles with different dimensions

Thixoforming temperature [ºC]	Dimensions of space holder particles	Density [g/cm^3]	$d_{cellular} / d_{compact\ alloy}$
620	coarse	0.53 ± 0.04	0.19
	fine	0.61 ± 0.04	0.22
630	medium	0.63 ± 0.04	0.22
	coarse	0.56 ± 0.04	0.20
	fine	0.73 ± 0.04	0.26
635	medium	0.57 ± 0.04	0.20
	coarse	0.63 ± 0.04	0.22
	fine	0.81 ± 0.04	0.29
640	medium	0.80 ± 0.04	0.28
	coarse	1.00 ± 0.04	0.35

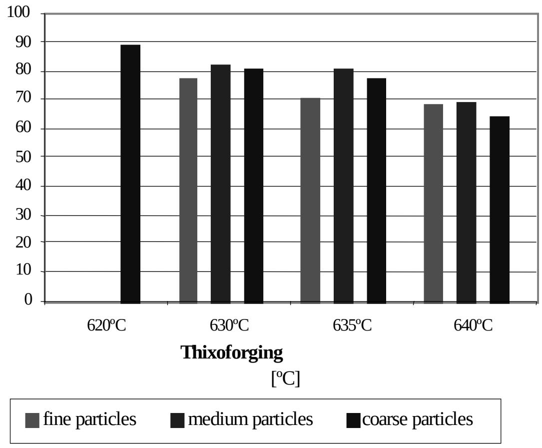

Fig. 9. Voids content in cellular A2011 produced by thixoforming at different temperatures into a layer of space holder particles of different dimensions

In general, voids contents resulted from different processing parameters are superior to 60% in samples produced in all conditions. Maximum value is 89% and minimum is 64%. It can be observed that increasing processing temperature voids content tends to decrease, as already detected in the density measurements, once this situation leads to thicker cell walls and increase in density values.

4. Conclusions

Results showed that the proposed process to produce cellular A2011 based on thixoforming of the alloy into a layer of NaCl particles as space holders is perfectly feasible and can result in reliable products. Complete washing out of the particles is possible since the porous are interconnected, which characterizes the material as sponges. Density and volume of voids presented are appropriated for typical cellular metals. In the analyzed conditions the influence of the size of space holder particles in the infiltration of the thixotropic alloy was not sensitive, unless the liquid fraction in the semi-solid is low. A critical parameter to be controlled in the process is the liquid fraction in the semi-solid. In situations where liquid fraction is small, infiltration is jeopardized leading to incomplete filling and compression of the space holder particles, resulting in weak cells walls and the presence of voids with big dimensions in the material.

Therefore, with proper temperature control good quality products can be obtained in a simple, low cost and easily controllable process.

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