Concerns on the development of the amorphous alloys in bulk and ribbon form

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1. Introduction

The discovery of the amorphous structure is the merit of the American professor Pol Duwez. In 1960 he obtained „metallic glass” in the Au-Si system using a rapid cooling method of metallic melt (drops) on a cooled substrate.

The amorphous structure is characterized by a disorderly arrangement of atoms in space. In the case of amorphous metals, the atoms distribution in space is not completely random, but groups of neighbor atoms meet an arrangement due to chemical or topological constraints. Therefore, the amorphous state is characterized by lack of long distance order in the spatial arrangement of the atoms and a certain order only at short distance.

A schematic representation of the amorphous metal structure is shown in Figure 1. Considering a short distance atomic arrangement (Fig. l.a), in case of crystalline structures it is multiplied in space on three directions, leading to an orderly arrangement in the volume of material (Fig. lb). In case of amorphous materials, this atomic arrangement at short distance, called „cluster” is distributed randomly in the volume of material, leading to long-range disorder atomic arrangement (Fig. l.c).

It is also important to define the term „metallic glass”. For solid materials, glass is the main amorphous substance. Up to the discovery of amorphous metal alloys, as defining amorphous materials were considered the glasses obtained by cooling at a rate of several degrees per second of fused silica.

During cooling, atoms or groups of atoms keep a certain disordered distribution from the liquid (melt). Therefore the term „glass” includes all of amorphous states obtained by cooling of melts, which is the reason they also called metallic glasses.

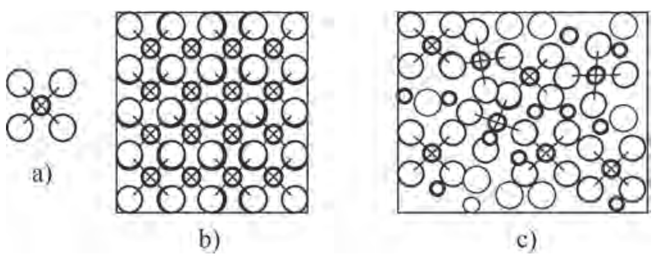

Figure 1. Schematic representation of the amorphous structure.

In the case of metallic materials, the formation of amorphous state is influenced by thermodynamic factors, which favour the liquid state versus crystalline phases, and by kinetic factors, which inhibit the crystallization [1].

One of the termodynamic factors is the reduced glass transition temperature T_{rg}, defined as the ratio between the glass transition temperature T_g and the alloy fusion temperature, T_f. The glass transition temperature is defined as the temperature which corresponds to the ideal situation when the viscosity would became infinite, and the specific volume equal with the specific volume of the crystalline solid. The forming tendency of metallic glasses is favourised by a high value of T_{rg}, this presuming a high value for T_g and a low value for T_f [1].

Another important termodynamic factor is the geometric factor. This factor is referring to the atomic size order, expressed as ratio between the atom radius of the majority component (r_A) and the atom radius of the minority component (r_B). A considerable difference between the atoms sizes of the components is necessary in order to facilitate the metallic glasses. Usually, r_A/r_B < 0,88 or r_A/r_B > 1.12 [1].

Also from termodynamic factors category are the electronic factor, which express the valence difference between the components that forms the alloy, and the electrochemical factor which refers to the electro-negativity difference between the alloys components .

The elements that favor the formation of metallic glasses tend to be located in different regions of the periodic table, so between the alloy components can be significant valence and electronegativity difference, but not too much [1].

The kinetic factor determinant in metallic glasses formation is the critical cooling rate for amorphization. It is defined as the minimal cooling speed necessary to obtain the glass transition by suppression of melt crystallization. As low is this critical cooling rate as better is the capacity of amorphization of the alloy [1].

These factors that favourise the amorphization depends on the chemical composition of the alloy. Choosing of the favourable composition domains in order to form the amorphous alloys, can be made using the equilibrium diagrams, the chemical composition accomplishing the following conditions [1]:

• the chemical composition range whereon the amorphous alloy is formed has to be placed in an equilibrium phase diagram zone where the liquid phase should be stable at low temperatures (a domain which contains eutectics or easily fusible compounds);

• the phase equilibrium diagrams of the alloys systems which form metallic glasses have to present small or even null solubility of components in terminal solid solutions, because of a free positive enthalpy which helps the formation of solid solutions;

• the alloys systems which form metallic glasses have to present intermetallic compounds, because the existence of more very stable intermetallic compounds with high complexity of the crystalline lattice, in a certain composition region of the phase diagrams region is, in a special way, complementary with metallic glasses formation in the other part of the phase equilibrium diagram.

2. Amorphous alloys in ribbon form

2.1. Obtaining methods

In order to obtain amorphous alloys in ribbon form having different sizes, high efficiency and an adequate reproducibility, ultrarapidly quenching method on a cylinder in rotation moving is used. This method is also known as „melt spinning" method. The main elements which interfere by elaboration using this method are schematically presented in Figure 2 [1].

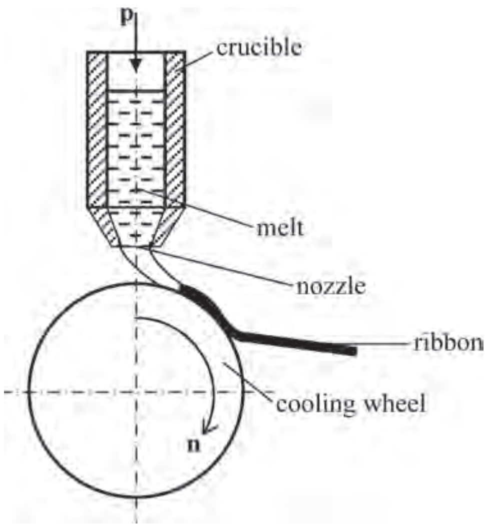

Figure 2. Schematic of the melt-spinning method.

The master alloy, having crystalline structure and a chemical composition favourable for amorphization, is melted into a crucible and forced to pass through the ejection nozzle orifice, falling on the cooling wheel surface, being in rotation movement.

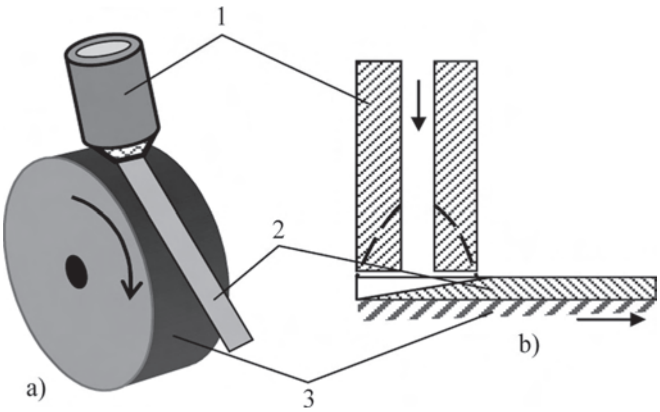

Figure 3. Schematic representation of planar flow casting process a) general view; b) detail of the orifice nozzle: 1 - crucible, 2 - ribbon 3 - substrate (cooling wheel).

Narasimhan had the idea of placing the ejecting nozzle in very close distance from the surface of the wheel (a fraction of a millimeter), thus providing a mechanical constraint for the bath and minimizing the perturbations [1]. In this configuration the melt quantity is maintained constant (the old metallic bath drew with dotted line in Figure 3.b and the obtained ribbon geometry is improved. This method is called „planar flow casting". The nozzle (figure 3.b) can be used without to limit the ribbons width, thus opening the way to the industrial production.

Using industrial installations (Figure 4), ribbons with 1 meter width were obtained. [1].

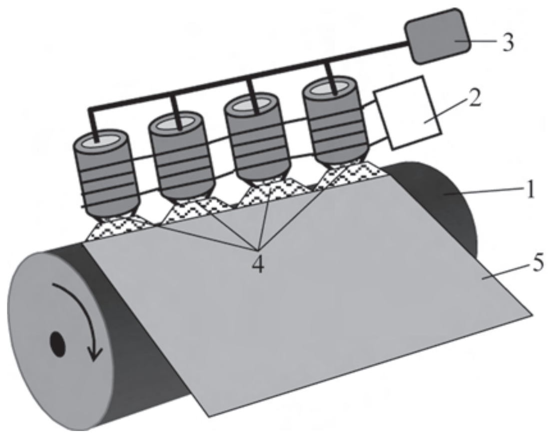

Figure 4. Schematic representation of an industrial installation for the production of wide ribbons 1 - water cooled wheel, 2 - induction furnace, 3 - melt alimentation system, 4 - orifice nozzles, 5 - ribbon.

A high number of published papers mention the existence of some main parameters of the process (the optimal values are presented in Table 1) as well as their correlation in order to obtain ribbons with desired geometry.

Table 1. Primary parameters and their optimal range [1].

Parameter	Units	Optimal range
Surface velocity, v	m/s	15 – 35
Ejection pressure, p	mbar	100 – 600
Driving gas		Ar
Nozzle width, l	mm	0.3 – 0.8
Distance roll surface - orifice	mm	0.4 – 1

Therefore, the dependency between the thickness *g* of the as-quenched ribbons obtained and the main process parameters ejection pressure *p* and angular speed *v*, is expressed by the following relation [1]:

$$g = \frac{k1}{v} \cdot \sqrt{\frac{p}{k2} + k3} \tag{1}$$

where: *k1* - depends on the rectangular cross-sectional area of the orifice;
k2 - depends on the density of the melt;
k3 - is a function of height of the liquid column above the orifice.

2.2. Ferromagnetic amorphous alloys

In the amorphous state, characterized by lack of ordering in the arrangement of atoms, there is a magnetic ordering state in which magnetic moments are arranged more or less parallel, which is the cause of a strong spontaneous magnetization. Field intensities of only a few mA/cm are sufficient to produce magnetization.

The soft amorphous alloys are represented by iron, cobalt or nickel alloys with another metal or metalloid.

Amorphous metals from Fe-B-Si-C system presents a high iron content (80-85%) and have a saturation magnetization comparable with the silicate steels (1,6...1,9 T) unde a very low coercive field (1... 6 A/m). Now the best set of magnetic properties related to the unitary cost is given by the metallic glass $Fe_{81}B_{13,5}Si_{3,5}C_2$, commercially offered by Allied Corporation under the name of „Metglas 2605 SC".

The amorphous alloys from Fe-Ni-Si-B system are characterised by a content of 50-60% iron, 14- 40% nickel, boron and silicon in rest for raising the amorphization capacity. These alloys presents high magnetic permeability rivaling with permalloy. Thus, can be obtained relative permeability of 60,000...250,000, at a saturation magnetization of 0,8T.

The amorphous alloys from Co-Fe-Ni-Si-B system have a non-value magnetostrictiv effect and also high magnetic permeability which is constant on a wide domain of frequency (20Hz...20kHz).

The magnetic properties of these amorphous alloys could be improved by application of some magnetic field or under tension annealing. Therefore, the magnetic hysteresis cycle can be easily modified as it can be seen in Figure 5 [1].

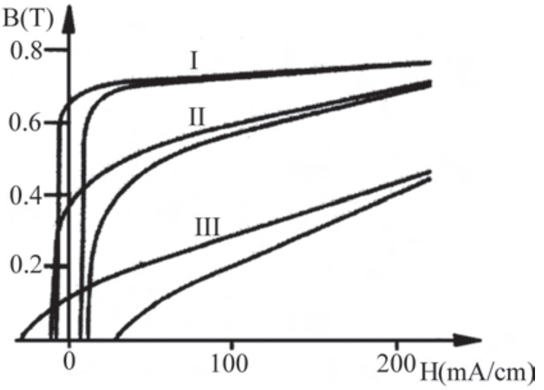

Figure 5. Hysteresis cycles - B=f(H) - by an alloys from Fe-Ni-Mo-B-Si family, obtained after different heat treatments: I - annealing in longitudinally magnetic field; II - annealing with rapid cooling; III - annealing in transversally magnetic field.

These magnetic properties associated with a high electrical resistance make these alloys (some examples are presented in Table 2) to present low magnetic losses and thus to be used in many applications.

Table 2. Magnetic characteristics of amorphous alloys [1].

Chemical composition of the alloy % at	B_s [T]	H_c [A/m]	μ_{max} [Gs/Öe] x 10^3
$Fe_{80}B_{20}$	1.58	4.0	320
$Fe_{78}Si_{10}B_{12}$	1.44	3.5	300
$Co_{65.7}Fe_{4.3}Si_{17}B_{13}$	0.53	0.48	5500
$Co_{61.6}Fe_{4.2}Ni_{4.2}Si_{10}B_{20}$	0.54	0.16	1200
$Co_{69.6}Fe_{4.6}Mo_{1.8}Si_8B_{16}$	0.63	-	1000
$Fe_{40}Ni_{40}B_{20}$	1	9.0	2000
$(Fe_{70}Co_{20}N_{10})_{90}Zr_{10}$	1.57	5,0	-
$Fe_{82}B_{10}Si_8$	1.52	7.0	200
$Fe_{40}Ni_{40}P_{14}B_6$	0.78	2.0	1100

Thus, these amorphous alloys elaborated in ribbons form are used as ferromagnetic core at high power transformers, in construction of induction coils, magnetic shielding and electronic devices.

Own research showed the possibility of obtaining amorphous alloys with soft magnetic properties from other families. Thus, we studied the Fe-Cr-P family, in order to obtain such ferromagnetic alloys with high strength and high corrosion resistance. These alloys 70...75% at. Fe, 5 ... 10% at. Cr, and the rest of P and other metalloids, to ensure the capacity of amorphization and the magnetic properties desired. Following the optimization of chemical composition and the process of elaboration, amorphous ribbons were obtained with thicknesses ranging from 18 to 20 µm and widths up to 2 mm, with high

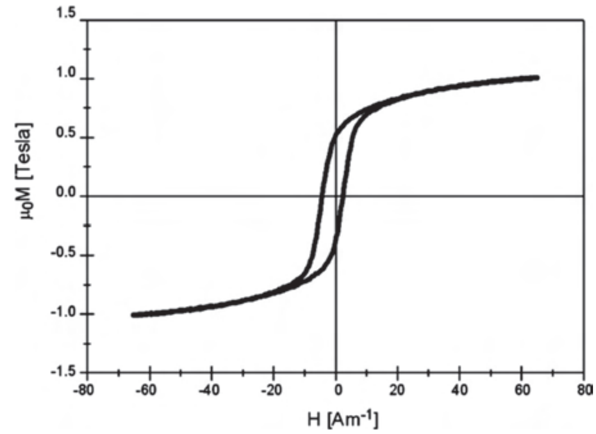

Figure 6. Hysteresis cycle of $Fe_{75}Cr_5P_{12}Si_5C_3$ alloy.

magnetic properties (magnetic saturation induction of 0.9 ... 1 T, coercive field 8 ... 10 A/m). The hysteresis cycle of such an alloy from this family is presented in Figure 6.

2.3. Amorphous alloys for brazing

One of the most important applications of amorphous alloys is manufacturing the ribbons for soldering and brazing. Most demanding technical field is the brazing the stainless steel components. Brazing alloys used for this purpose are the nickel alloys with additions of sufficient boron, silicon, carbon or phosphorus to reduce the melting temperature to ≈ 900 - 1100°C.

In cast form these alloys contain extensive and fragile phase of large crystals, making them rough- forming. Therefore, they are mechanically sprayed and applied mixed with 50% organic binder as a transfer tape. Using a brazing ribbon leads to the desired resistance bonding on the one hand, the variable losses during brazing cycle and on the other hand, a inevitable variation in the composition of the used powders.

Using melt-spinning method these alloys can be obtained as amorphous ribbons sufficiently ductile to mold the contours of parts [2, 3]. They can be cut or stamped to desired form minimizing losses of material. Their uniformity of composition leads to a uniform melting and safer control of the brazing alloy penetration between the pieces that blend; the dissolution of the base material is stronger and alloying by diffusion with brazing alloy components is best achieved. These effects, plus other considerations such as reduced thickness of the brazing strip (≈ 1/3 of conventional binder strip thickness), its thickness uniformity, absence of organic binder, finally producing a brazing joint narrow, stronger, more ductile and better corrosion resistance. Brazing technology becomes simpler, faster and with reproducible results.

Own research [4, 5] has demonstrated the possibility to obtain ribbons solder alloys from Fe- Ni-Cr-Si-B-Co family, Sudarea şi Încercarea Materialelor

Laser beam material processing

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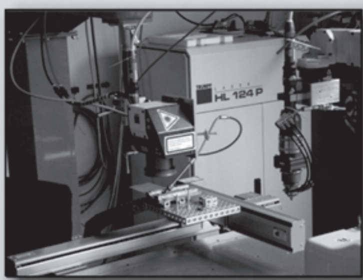
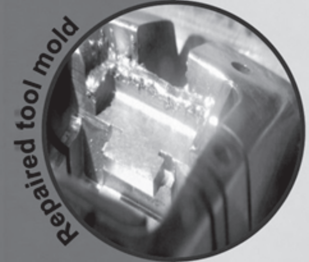


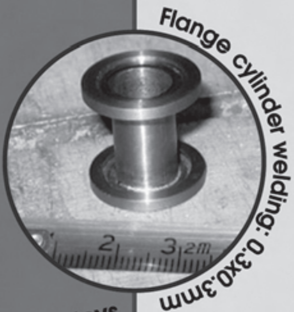
Pulsed Nd:YAG laser, maximum pulse power: 5kW; maximum average output power: 120W; 3 optical heads

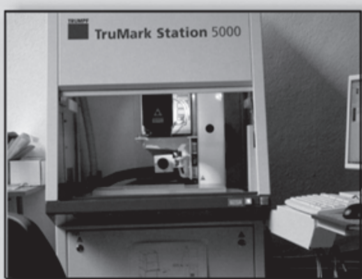
- micro-welding / micro-cutting
- programmable focusable optics
- superficial heat treatment
- spot micro-welding
- engraving

TLF1500 CO_2 laser cutting and welding workstation

- cw laser
- 1.5kW maximum output power
- xyz working table: 400 x 600 x 240mm

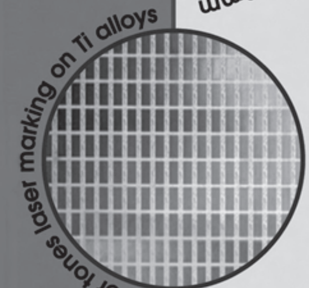






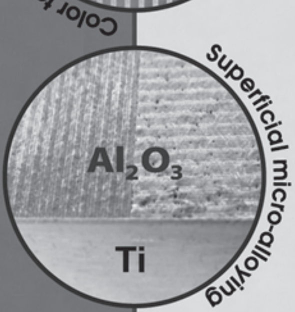
Metallic and non-metallic laser marking and engraving workstation

- high precision machining with minimum influence of the machined component
- maximum marking dimension: 110x110mm
- marking of: logos, graphical objects, ID codes, barcodes, data matrix, etc.
- minimum spot size: 40 µm.



Micro-welding / micro-cutting laser beam modulus

- pulsed Nd:YAG laser with beam expanding system and processing optics with micro-welding and micro-cutting characteristics
- minimum spot size: 30µm
- programmable parameters: pulse duration (0,02-20ms) and pulse repetition frequency (0,1-1000Hz);
- maximum pulse power: 4kW
- maximum average output power: 100W;
- processing optics focal length: 50mm



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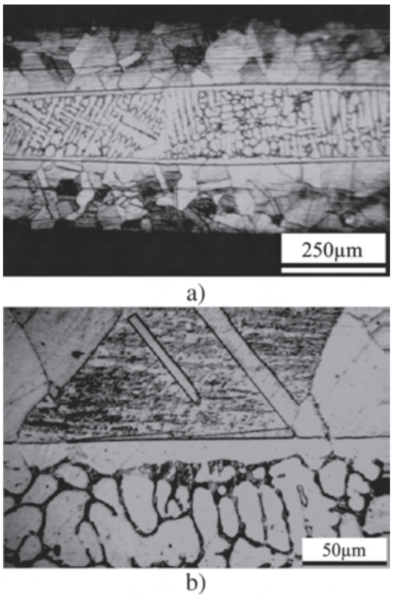
with amorphous structure and thickness of 20 mm and width of 1 mm. The brazing alloy behavior was monitored realizing overlapping solders of austenitic stainless steel bands with a size of 0.2 x 15 mm, during brazing in a vacuum oven.

The chemical composition and the mechanical properties of the base material, according to the quality certificate, are presented in Table 3.

Table 3. Chemical composition and mechanical properties of base material.

Chemical Composition [% Weight]							Mechanical Properties		
C	Mn	Si	P	S	Cr	Ni	R_{p02}	R_m	A_5
							[N/mm²]		[%]
0.05	1.51	0.52	0.035	0.007	18.09	9.13	260	642	65

The metallographic analyze of the the brazing highlights the base material's structure consisting of polyhedral grains of austenite, in which appear macle, so a specific structure of an austenitic stainless steel (Figure 7). The joining assembly is characterized by a single-phase dendritic structure, (Fig. 7).



a)

b)

Figure 7. The microstructure of bonding.

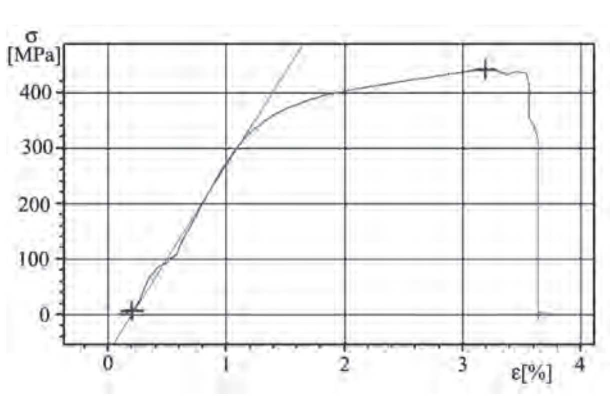


Figure 8. Traction curve of brazing bonding.

For a complete characterization, the brazing were tested to breaking shearing. The tests were performed on a Instron 5584 machine.The traction curve is presented in Figure 8. It can be noted that the breaking is ductile, the material suffers a plastic deformation before breaking.

The results show that the tensile shear of the bonded joint (442 MPa) exceeds the yield strength of the base material (260 MPa).

Recent research [6] showed the possibility to obtain amorphous alloys based on Cu solder. Our experiments allowed obtaining amorphous alloys of Cu-Ni-Sn-P family, as ductile, continuous, geometrical uniform ribbons, with 20 µm thickness and 4 mm width. The presence of phosphorus is required because this element provides the alloy's amophizations and ensures the etching during the brazing. Nickel improves the mechanical properties and the corrosion resistance, while the presence of the Sn reduces the melting temperature of the alloy.

To test the behavior of the alloy's brazing were developed glued joints by bonding method in the resistance of the pressure points; because it is a quick solder method, which provides high heating and cooling rates, in order to avoid the precipitation in the joint assembly of the intermetallic compounds.The bonding was achieved by overlapping the combination of two copper bands with thickness of 1 mm and width of 15 mm, without solder flux.

The joint assembly was subjected to metallographic analysis and traction test.

The microscopic images show a structure with a single phase, without precipitation of intermetallic compounds, geometrical uniform (Figure 9).

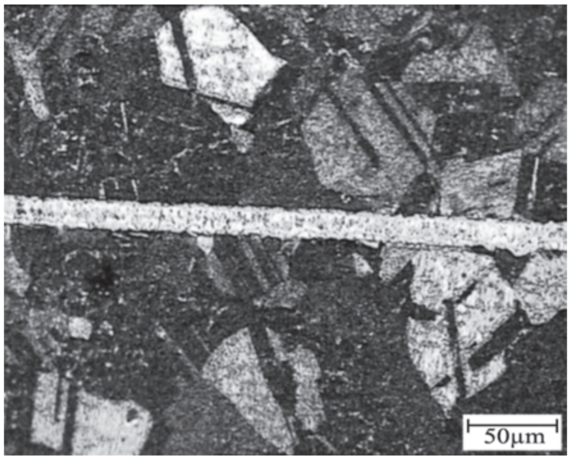
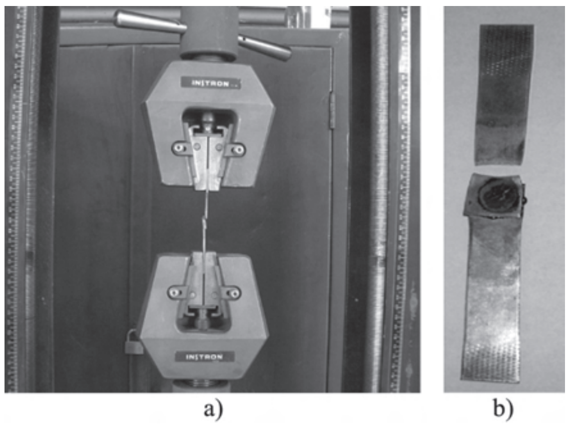


Figure 9. The microstructure of bonding.



a)

b)

Figure 10. Shear test: a) sample testing; b) broken sample.

The traction test was performed on an Instron machine. On the tested samples it was noted that the joint assembly is not damaged, the breaking is produced in the base material (Figure 10 b), which leads to the conclusion that the joints have excellent resistance to shear.

3. Bulk amorphous alloys

Due to their properties, the amorphous alloys are attractive for many practical applications, therefore the need to make products that meet various industrial applications, has led the research to increase processing of bulk amorphous alloys. Recent research [7, 8, 9] discovered of multicomponent amorphous alloys (based on Zr, Pd, Pt, Mg, Ti), that are characterized by low cooling critical speed (from 0.1 to 10^3 K/s), which allowes to obtain products with thicknesses of tens of millimeters.

To achieve this performance, it is necessary to folow three empirical rules, so the glass forming ability (GFA) could be as high as possible: (i) multicomponent system consisting of more than three elements; (ii) significant difference (beyond 12 %) in atomic size ratio among the three main constituent elements; (iii) negative heat of mixing among the three main constituent elements. The researches [9] showed that to obtain a high degree of amorfization it is necessary that the low glass transition temperature (given by the ratio of the glass transition temperature and the melting temperature of the alloy) to be high and the difference between the temperature of the glass transition and the crystallization temperature of the alloy to be 50 K.

3.1. Obtaining methods

The most used methods for obtaining massive amorphous alloys are based on melt solidification. We have developed several methods: casting in copper mould, die casting, suction casting and centrifugal casting.

Simple casting copper mould (Figure 11) involves the melting of the master alloy and ejected it directly into a copper mould which has the shape and size of the desired product. Usually, the casting is realized in a closed chamber with a protective atmosphere.

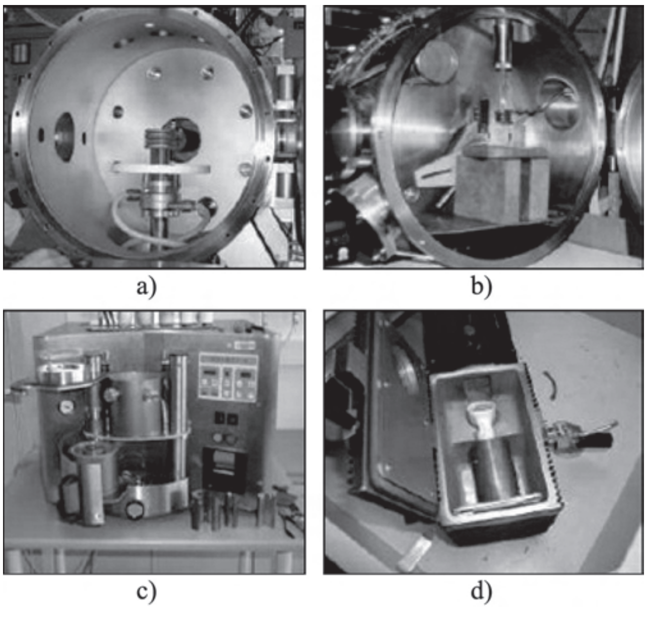


Figure 11. Casting methods for obtaining bulk amorphous alloys.

High pressure casting (Figure 11b) is also realized in a copper mould , but in this case the molton alloy is injected with pressure in the cavity. This process allows higher cooling rates and therefore a greater variety of products compared with the previous method.

In suction casting (Figure 11c)is required that the molten alloy is drawn into the cavity of the copper matrix. In this case, the speed of cooling rate is higher than high pressure casting. For complex parts it can be used the mixt process consisting of high pressure and suction casting. In this case the molten alloy is ejected and simultaneously absorbed into the copper mould cavity, ensuring its proper filling and good compactness of the piece obtained.

The centrifugal casting (Figure 11d) involves the rotation of the copper mould using an electric motor. The melted alloy is injected into the mould cavity and designed by a centrifugal force on the walls. This method is typically used to obtain tubular products.

3.2. Ferromagnetic bulk amorphous alloys

The most known bulk amorphous ferromagnetic alloys are from the Fe-(A1, Ga)-(P, C, B, Si) system, which could be processed as amorphous rods up to 2 mm diameter. These alloys are characterized by excellent soft magnetic properties (magnetic saturation induction of 1.1... 1.2 T, coercive field of 2...6 A/m and relative permeability of 7000 at a frequency of 1 kHz) [9]. Also, bulk amorphous alloys were obtained as rods with diameters up to 12 mm from Nd-Fe-Al system, characterized by hard magnetic properties (coercive field of 300 ... 400 kA/m) [9].

Own research [10, 11] focused on achieving bulk amorphous ferromagnetic alloys from Fe-Cr- P-Ga-Si-C family. Using copper mold casting under high pressure of the Fe70Cr6Ga4Pi2Si5C3 alloy were obtained 1 mm in diameter rods with amorphous structure (Figure 12).

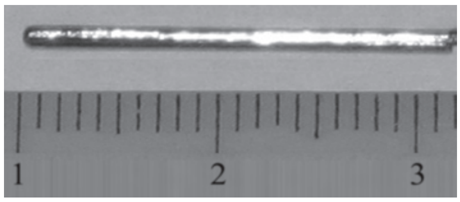


Figure 12. Rod with 1 mm diameter.

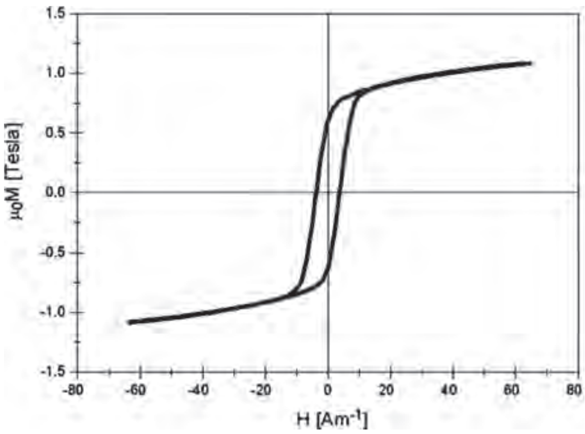


Figure 13. Hysteresis cycle of the amorphous rod.

As the hysteresis cycle of the amorphous rod produced (Figure 13) these alloys have good soft magnetic properties (magnetic saturation induction of 1.1 T, coercive field of 8 A/m).

An application of these alloys is to produce a series of magnetic shields for sensors that work in aggressive environments.

To obtain products in socket form with a diameter of 7 mm, height of 15 mm and wall thickness of 1 mm, it was designed a copper mould shown in Figure 14.

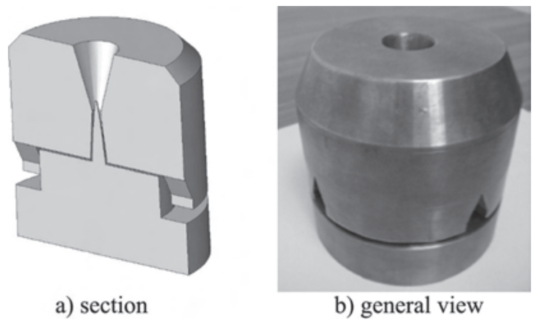


Figure 14. Copper mould.

After casting in the copper mould, a socket product was obtained, that is compact, homogeneous, without traces of oxides on the surface. (Figure 15)

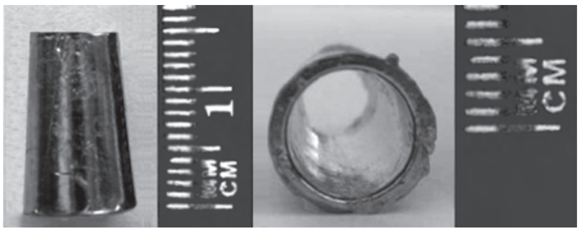


Figure 15. The obtained product.

To test the screening ability of the socket, was performed for comparation, a similar socket of permalloy.

The shielding capacity was determined by measuring the inside magnetic field when a exterior magnetic field is applied.

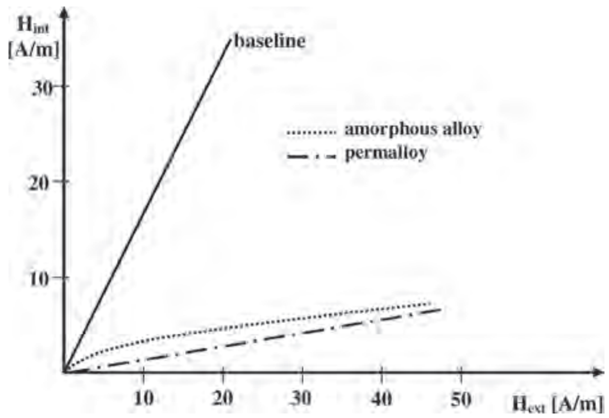


Figure 16. Screening capacity by measuring the inside magnetic field.

It can be noticed that amorphous alloy has a high magnetic shielding capacity compared with crystalline alloys commonly used.

4. Conclusions

Amorphous alloys are still a subject of advanced research, as the result of a set of properties that make them particularly attractive in many industrial applications

Amorphous alloys in ribbons form, with thickness up to 60µm and widths up to 1 m are produced currently on an industrial scale using „melt-spinning" and „plannar flow casting" methods, successfully used in electrical, electronics applications and at the manufacturing of composite materials and brazing alloys.

The challenge today is to obtain bulk amorphous alloys as products, in mm order thickness that can be used in industrial applications. The chemical composition was optimized for some alloys based on Zr, Pd, Pt, Mg, Ti, Fe, Nd that are characterized by low cooling critical speeds (from 0.1 to 10^3 K / s), which allow to obtain products with thicknesses tens of millimeters by different methods of copper mould casting (simple casting, high pressure casting, suction casting, centrifugal casting).

Among of amorphous alloys, the bulk ferromagnetic amorphous alloys are a new challenge, due a huge applied potential.

In this context are registered the own researches performed on Fe-Cr-P-Ga-Si-C alloys, which led to the obtaining magnetic shields in socket form, with wall thickness of 1 mm, which can be used for a number of sensors working in corrosive environments.

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