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Self-fluxing amorphous Nickel-based alloys obtained by different techniques. Performance and technological difficulties

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Abstract. Amorphous metal alloys can already be considered advanced structural materials. This structure induces specific properties such as: high mechanical resistance and hardness, high bending ductility, high elastic modulus, superior resistance to corrosion and wear or, depending on the chemical composition, exceptional magnetic properties.
The family of self-fluxing alloys based on nickel has multiple applications: NiCrBSi powders are used with remarkable results in obtaining protective layers against corrosion and wear, strips and wires are successfully used as brazing alloys, etc.
In this paper it is presented the research carried out for obtaining and characterizing the amorphous NiCrSiB ribbons, through the melt spinning technique and the massive products (bulks) from the same family through mold casting and additive manufacturing using the Selective Laser Melting (SLM) technique

Keywords: self-fluxing alloys, amorphous structures, Copper mold casting additive manufacturing.

1. Introduction

Self-fluxing alloys are becoming more and more interesting due to their ease of application which involves plasma spraying and sintering. In general, self-fluxing alloys are produced by adding small quantities of carbon, boron or silicon to nickel, cobalt or iron-based alloys. By adding carbon or boron, the hardness and wear-resistance of the coating layer increases due to the precipitation of the carbides and borides from the matrix.[1], [2].

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Ni-based self-fluxing alloys are usually used in brazing stainless steels and super alloys or like materials which are resistant to different mechanisms of wear.

The increasingly widespread use of amorphous metallic materials is due to a combination of excellent properties like hardness, mechanical strength, and ductility, which are superior to crystalline metallic materials and have very high corrosion resistance [3].

Currently, a wide range of methods for ultra-rapid solidification of metallic materials is available worldwide. These methods allow obtaining small-sized products due to the need to ensure the critical cooling rate required for amorphization. It can be produced thin products with a thickness of 20-50 μm, such as, ribbons, powders, or fibers.

The problems related to the small size of the amorphous alloys have been partially solved by the development of bulk metallic glasses, which have a thickness of at least 1 mm and higher glass forming ability.

Additive manufacturing can be described as the process of joining or adding materials with the main objective of creating objects from three-dimensional model data using the layer-by-layer principle. Layer manufacturing technologies are known as rapid manufacturing or rapid prototyping. Compared to traditional manufacturing techniques, which need to remove material to fabricate the desired products, the additive manufacturing technique allows the creation of the final products by adding layers of material [4], [5].

This paper aims to present the research carried out for obtaining and characterizing self-fluxing Ni-based amorphous alloys, by methods based on rapid solidification of the melt and additive manufacturing.

2. Obtaining amorphous alloys from the Ni-Cr-B-Si family in ribbons form

2.1. Method and materials used

Self-fluxing Ni-Cr-B-Si alloys were developed for the brazing of stainless steels and Ni or Co based super-alloys. These alloys are usually alloyed with B, Si and P to form eutectics that decrease the fusion temperatures that are relatively high for Ni or Ni-Cr matrix. At the same time, the presence of these metalloids in the chemical composition of these alloys ensure good wettability and the self-fluxing property.

Considering the previous experiments [6] and the conditions of amorphization in order to elaborate these alloys in ribbons form with an amorphous structure, the following chemical compositions were chosen: $Ni_{68}Fe_3Cr_7Si_8B_{14}$ and $Ni_{61}Cr_{13}Fe_8Si_{10}B_7Co_1$.

Master alloys ingots with a diameter of 10 mm and a length of 30 mm were synthesized by the induction melting of the mixture of pure elements Ni, Cr, Fe, Co and Fe–B and Fe–Si ferroalloys in an argon atmosphere. After that, the master alloys were remelted four times to obtain a better homogeneity.

The Melt Spinning Casting (MSC) method was used to obtain the alloys in the form of continuous ribbons of 25 µm thickness and 1.5 mm width (Figure 1). This method which is already well-known involves the following steps [6,7]: (i) developing a master alloy with a chemical composition that has a high glass forming ability (GFA); (ii) re-melting and continuous casting of the master alloy on a rotating cooling roller.

Fig. 1. Macroscopic aspects of the obtained ribbons.

The amorphous structure of the elaborated alloys was examined by X-ray diffraction using an X'Pert³ Powder diffraction equipment, with the radiation of a Cu anode with a wavelength λ = 1.54 Å.

Differential scanning calorimetry (DSC) was used to investigate the thermal stability of the elaborated alloys. The analysis was performed with a Netzsch STA 441 Jupiter equipment using purified nitrogen for purge and a heating rate of 20 K/min. The glass transition temperature Tg, the crystallization temperature Tx and the melting temperature Tm were determined as the onset temperatures of the corresponding peaks.

2.2. Results and discussions

The diffraction pattern of the alloys developed in the ribbon form is shown in Figure 2. In both cases, it can be observed only broad peaks that are characteristic of an amorphous structure.

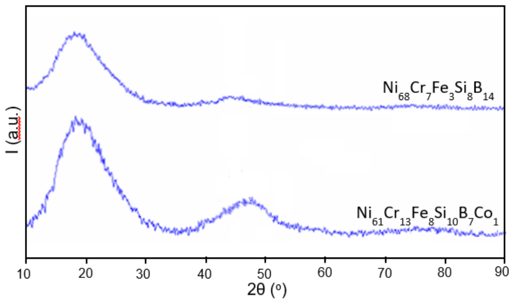
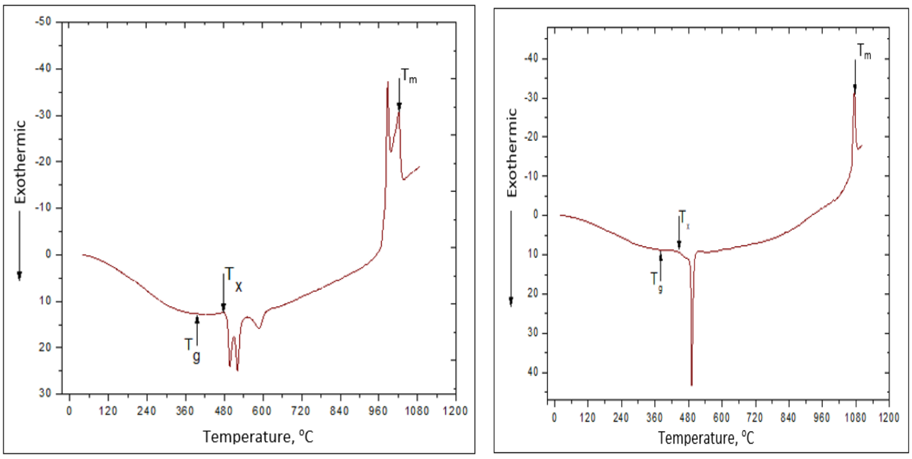


Fig. 2. X-ray diffraction patterns of the elaborated ribbons.

The DSC curves were obtained by heating 10 mg of the elaborated alloys from the temperature of 20 °C up to 1150 ºC.

It can be noted that the DSC curves reveal the presence of exothermic peaks which mark the crystallization events and confirm the amorphous structure of the elaborated alloys (Figure 3). Unlike the $Ni_{61}Cr_{13}Fe_8Si_{10}B_7Co_1$ alloy, which presents a primary crystallization (Figure 3b), the crystallization process of the $Ni_{68}Fe_3Cr_7Si_8B_{14}$ alloy is more complex, and the crystalline phase resulting from the devitrification of the amorphous phase is metastable and it turns into a more stable crystalline phase with the temperature increase (Figure 3a).



a) $Ni_{68}Fe_3Cr_7Si_8B_{14}$ b) $Ni_{61}Cr_{13}Fe_8Si_{10}B_7Co_1$

Fig. 3. DSC curves of the elaborated ribbons.

The glass transition temperature Tg, the crystallization temperature Tx and the melting temperature Tm for each alloy were determined and listed in Table 1. These critical transformation temperatures allow calculating the supercooled liquid region which describes the glass forming ability (GFA) of the amorphous alloys. The extension of the supercooled liquid region ΔTx, defined as the difference between the crystallization temperature Tx and glass transition temperature Tg, provides information about the thermal stability.

Table 1 Transformation temperatures for the elaborated ribbons

Alloy	**T_g [°C]**	**T_x [°C]**	**T_m [°C]**	**ΔT_x (T_x - T_g)**
$Ni_{68}Fe_3Cr_7Si_8B_{14}$	408	480	1020	72
$Ni_{61}Cr_{13}Fe_8Si_{10}B_7Co_1$	410	475	1070	65

It was found that both alloys have good thermal stability and quite high crystallization temperatures. The $Ni_{68}Fe_3Cr_7Si_8B_{14}$ alloy, has a slightly higher crystallization temperature (480 °C) than the $Ni_{61}Cr_{13}Fe_8Si_{10}B_7Co_1$ alloy (475 °C). Also, the parameter that defines the GFA has close values, slightly better value was noted in the case of the $Ni_{68}Fe_3Cr_7Si_8B_{14}$ alloy due to the presence of metalloids in higher proportions. By increasing the content of metalloids an increase in the atomic packing density of the liquid structure is favored [8]. The higher the atomic packing density is, the easier it is to obtain the amorphous structure.

3. Obtaining bulk metallic glasses from the Ni-Cr-B-Si family

3.1 Copper mold casting

This method refers to the casting of the molten alloy directly into a copper mold with various dimensions and shapes, such as circular or rectangular. Many of the amorphous alloys have been cast by this method which is usually carried out in a closed chamber with a protective atmosphere.

3.1.1 Method and materials used

In order to bulk metallic glasses, it is necessary to establish a chemical composition that ensures the lowest critical cooling rates of amorphization (from 0.1 to 10^3 K/s) [1]. Research carried out so far showed that optimizing the chemical composition will allow the obtaining of products with thicknesses larger than 1 millimeter. For that, it is necessary to follow three empirical rules [9]: (i) a 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.
By considering all these rules, the following chemical composition was chosen: $Ni_{68}Fe_3Cr_2Ga_4Si_5P_{14}B_4$. In comparison with the chemical compositions of the amorphous alloys obtained in the ribbons form, the addition of Ga and P increases the number of alloy components and improves the GFA.

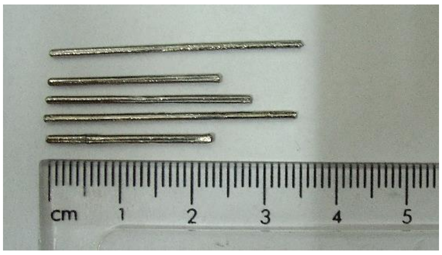


Fig. 4. Macroscopic aspects of the obtained rods.

Master-alloy ingots were prepared by induction melting a mixture of pure elements Ni, Fe, Cr, Ga, and Fe–B, Fe–P, and Fe–Si ferroalloys in an argon atmosphere. Cylindrical rods with a 1 mm diameter were synthetized by water-cooled copper mold casting method (Figure 4).
The amorphous structure of the as-cast samples was examined by X-ray diffraction using a Cu anode radiation, and the thermal stability was studied by DSC analysis using the same equipment and methodology as in the case of the characterization of the alloys elaborated in the ribbons form.

3.1.2 Results and discussions

In Figure 5 is presented the X-ray diffraction pattern of the $Ni_{68}Fe_3Cr_2Ga_4Si_5P_{14}B_4$ alloy and reveals only a broad diffuse peak without any evidence of crystalline phases.

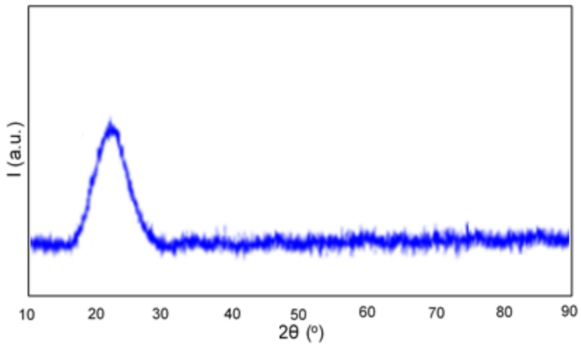


Fig. 5 XRD diffraction pattern of the elaborated rods.

The DSC curve of the as-cast $Ni_{68}Fe_3Cr_2Ga_4Si_5P_{14}B_4$ alloy is presented in Fig. 6. An exothermic peak is observed which marks the crystallization of the amorphous phase. As in the case of the other elaborated alloys, the critical transformation temperatures (T_g, T_x, T_m) were determined and the parameter that defines the GFA ΔT_x was calculated. The values are listed in Table 2.

Alloy	**T_g [°C]**	**T_x [°C]**	**T_m [°C]**	**ΔT_x (T_x -T_g)**
$Ni_{68}Fe_3Cr_2Ga_4Si_5P_{14}B_4$	320	400	1118	80

Table 2 Transformation temperatures for the elaborated rods

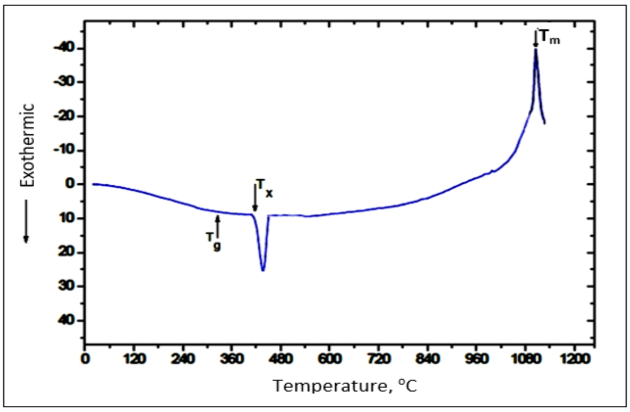


Fig. 6. DSC curve of the elaborated rods.

Lower thermal stability of the amorphous phase is observed compared to the alloys obtained in the ribbon form, but the supercooled liquid region ΔT_x is greater. Therefore, the presence of Ga and P led to the increase of the atomic packing density, thus favoring the obtaining of the amorphous structure. Also, the presence of P in the alloys chemical composition contributes to a deoxidizing effect of the melt [10], which can lead to suppression of heterogeneous nucleation, thus improving the glass forming ability.

3.2 Additive manufacturing

The explosive development of additive manufacturing technologies has led to a commensurate interest and their use in obtaining bulks with an amorphous structure. There are several additive manufacturing methods, the most well-known and used being "Selective Laser Sintering (SLS)" and "Selective Laser Melting (SLM)"

3.2.1. Method and materials used

Selective Laser Melting (SLM-Selective Laser Melting) is an additive manufacturing technique developed to melt and fuse metal powders using a high-power density laser. The principle of the SLM process starts with a building platform applied with very thin layers of metallic powders, which are completely melted later by thermal energy induced by one or several laser beams. The product obtained will have very low porosity, which makes it indicated for a wider range of applications. Recent research has also revealed the possibility of obtaining amorphous structures due to the higher cooling rates observed during the process.
During the experiments, the ORLAS Creator RA equipment with a laser power of 150W was used in the equipment of the Additive Manufacturing laboratory of the Westphalian University of Applied Sciences.

3.2.2 Results and discussions

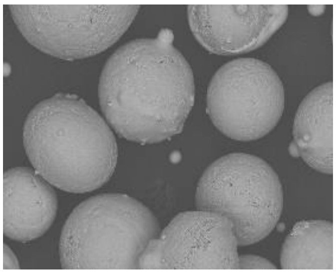


Fig. 7.SEM images of powders of NiCrBSi used in SLM (magnitude x1000)

Relatively uniform powders from self-fluxing alloys from the NiCrBSi family were used as sample materials (Figure 7). The experiments had a preliminary character following the multiple technological difficulties encountered.
Samples of size ø 10 x 5 mm were obtained with the chemical composition ($Ni_{53}Cr_{15}Fe_4Cu_2 Mo_2B_{14}Si_7C_2$ (Figure 8). Laser scanning velocity influence (with values in the range of 400-700 mm /s on the quality and structure of the manufactured samples was studied.

The macroscopic analyzes revealed the presence of micro-pores and micro cracks in a variable proportion depending on the parameters used (Figure 9).

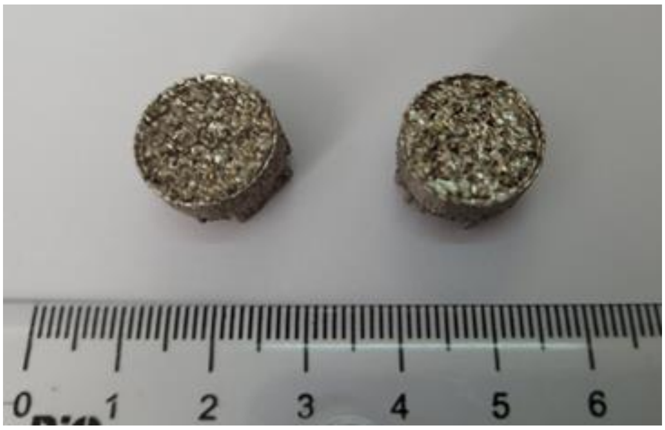


Fig. 8. Images of obtained samples.

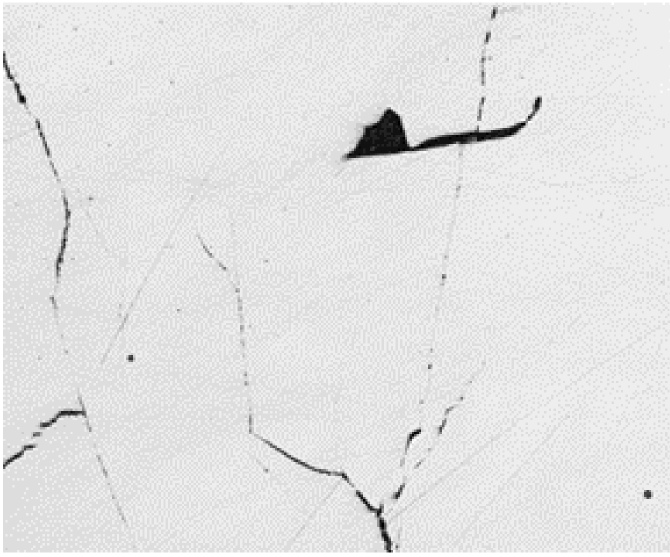


Fig. 9. Pores and micro-cracks
observed (magnitude x20).

The X-ray investigations revealed a predominantly crystalline structure (Ni-based phases). The amorphous phase was identified by additional alloying with Gallium in proportions of 3-4%. In this case the scanning velocity is set to minimum values.
A few comments are required:
Obtaining BMG products through this technique, although it theoretically offers the possibility of manufacturing large-sized BMGs and components with complex geometries, faces several difficulties [11] some of them being confirmed by own experiments:

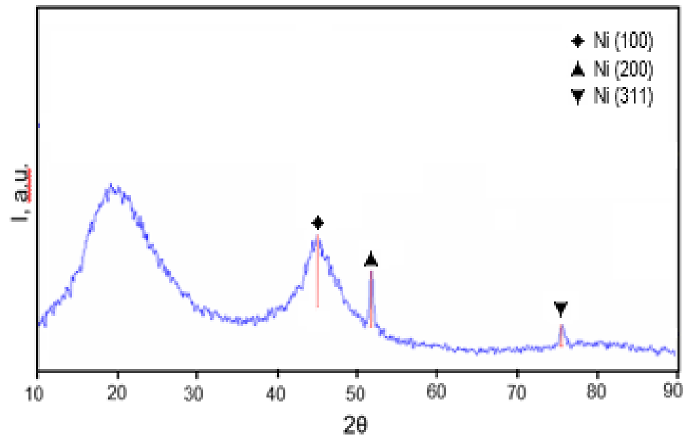


Fig. 10. XRD diffraction pattern for the elaborated alloy.

Amorphous structures can only be obtained for compositions with a high glass forming ability and a high thermal stability (during the addition of each new consecutive layer, the temperature of the previous layer increases, which can lead to its crystallization). In the present case, the introduction of Gallium in 3-4% percentages led to favoring the appearance of an amorphous phase - Although low deposition speeds were applied and relatively uniform powders were used, the formation of micro-pores and micro-cracks could not be avoided.

- it is necessary to continue the research for the optimization of the analyzed parameters and the identification of others that influence the quality and structure of BMG.

4. Conclusion

The present research revealed that amorphous alloys in the form of continuous ribbons Ni-Cr-B-Si family can be obtained using the melt spinning casting method.

Furthermore, bulk metallic glasses with thicknesses around 1mm were obtained using copper mold casting.

The addition of Ga and P in the chemical composition of the analyzed alloys leads to an increase in the amorphization capacity of BMG.

Obtaining quality bulk metallic glasses through additive manufacturing faces major difficulties. For self-fluxing alloys based on Ni-Cr-B-Si, additional alloying with chemical elements (Ex Ga, Y) is required to increase GFA and the technologies and additive manufacturing processes must be improved.

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