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INSTITUTE OF ENGINEERING PROCESSES AUTOMATION
AND INTEGRATED MANUFACTURING SYSTEMS

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THE SELECTED MANUFACTURING PROBLEMS OF THE BULK METALLIC GLASSES

Abstract: In this article selected problems that occur during the manufacture of bulk metallic glasses have been discussed. A number of different techniques to synthesize bulk metallic glasses (BMG) alloys have been developed. These developments have been occurred in different laboratories, for some specific applications or materials. In this paper the analysis of glass transition factors and the associated technological problems have been presented. The observations and gained experience during the preparation of iron-based and zirconium-based bulk metallic glasses prepared by die pressure casting method were the basis for this elaboration.

1. Introduction

The bulk metallic glasses belong to the group of modern engineering materials which are increasingly used in high technology. The BMGs are those metallic glasses that have a section thickness of at least a few millimeters. They have many common structural features, i.e. structure, which decides about influence on their properties [1].

The crystal structure is characterized by stability and in the metal at a relatively low supercooling temperature from the liquidus temperature is formed. Under specific circumstances, i.e. under very intensive cooling conditions, some alloys can be performed to solid state without crystallites. In this situation, the atoms adopt random position which is characteristic of the liquid. The metals with disorder structure are called amorphous or metallic glasses. The metallic glasses are usually multicomponent. The properties of alloys of the same composition in the amorphous state are different to the crystalline state. The BMG are characterized by excellent mechanical, physical and chemical properties due to the high chemical homogeneity of the structure. The BMGs exhibit high strength, high hardness and good corrosion resistance [2, 3, 4].

2. Glass forming ability and formation of bulk metallic glasses – rules, conditions, parameters

This paper is intended to present the selected problems of the bulk metallic glasses manufacturing. The success of bulk glassy alloy producing with better properties and require structure by the use of special designed casting method is very encouraging for the future development of these materials.

The scientists D. V. Louzguine-Luzgin et al. [5] have divided factors influencing the amorphization possibilities which result from the characteristics and properties of the produced alloy and the factors that depend on the conditions of the manufacturing process. Proper selection of the chemical composition and production parameters control make high glass forming ability alloys preparation possible. It is an important to point out that the occurrence of many phenomena, the influence of some parameters or the inability to control over the emerging problems can't be fully explained.

The effect of chemical composition on the ability of the glass transition hasn't yet fully understood. On the basis of the study, the scientists have identified a number of empirical conditions that should fulfilled in order to obtain metal alloys with a high glass forming ability. It was found that proper selection of the initial material components should lead to formation of the eutectic alloy. The composition of the alloy should be close to the low melting eutectic composition. Ultimately, it can be noted that receiving bulk amorphous alloys is mainly based on the use of three empirical rules formulated by A. Inoue [4, 1].

A high homologous glass transition temperature T_{rg} and reducing critical cooling rate are further conditions to facilitate the preparation of the amorphous phase. Reduced glass transition temperature T_{rg}, defined as the ratio between the glass transition temperature T_g and liquidus temperature T_l is the main parameter determining the glass forming ability of the tested alloy. T_{rg} value greater than 0.6 indicates the large glass forming ability of alloys. Thermal parameters should strive to increase the temperature T_g, while reducing the value of temperature T_l. Increase of T_{rg} cause reducing amount of the heat which should be collected from the liquid state alloy [1, 4].

The next parameters, the viscosity and diffusion coefficients are a kinetic parameters that affects of the glass formation. The results of the tests indicate that the lowering temperature of molten alloy below the liquidus temperature T_l leads to a rapid increase in melt viscosity [5].

The cooling rate is main parameter that influences the structure of the solidified metallic alloy. The limitation of nucleation is necessary during the manufacture of BMGs. Surface energy should be increased, the formation and growth of crystalline phases should be stopped and the diffusion should be restricted.

The formation of crystalline phases is result of solidification of the material in equilibrium condition. When cooling rate is increasing then metastable phases were formed. The limitation of atom mobility is occurred during solidification. The use of a cooling rate greater than the value called the critical cooling rate R_c of the alloy leads to the formation of amorphous phase. R_c values depend on the material composition. This parameter determines the BMG thickness. The value of the critical cooling rate is in the range of 0.10 K/s for alloys on the palladium base to 10^6 K/s for alloys on iron, cobalt or nickel based [4, 5].

The results of tests indicates that different systems of multi-component alloys present different values of R_c. It involves the selection of appropriate technology of amorphous materials production, which provide the favourable parameters to the formation of the desired structure. The formation of BMGs in the form of elements with large cross sections is a particular difficulty. The cooling rate decrease with the increase in size of the samples.

The chemical affinity for oxygen elements in the alloy is the major problem hindering the large-scale production of amorphous materials. The chemical affinity phenomenon can affect the growth of contaminants, which can form a heterogeneous nucleation of crystallites. These pollution significantly reduce the glass forming ability of alloys. Therefore, it is crucial to provide a protective atmosphere during the melting and casting processes of the BMGs.

The each of produced BMG system alloy requires individually study procedure for the preparation of the ingot. The proper preparation of the initial alloys, should be provided a uniform distribution of atoms of the constituent elements in the liquid phase. Separation of the constituent elements significantly limit the ability of the glass transition alloys. At this stage of preparation, multi-stage casting process (when the melting points of elements are different) or repeated re-melting process to homogenize the chemical composition are often used.

A very high costs of alloying element is the next fundamental problem limiting the production of BMG. It is advisable to use the elements of high purity. Moreover, the alloying agents to obtain elements with dimensions greater than 1 mm are required i.e. expensive rare earth elements (Er, Y) or Zr.

3. The production of $Fe_{71}(Nb_{0,8}Zr_{0,2})_6B_{23}$ alloy by the pressure die casting method

Fe-based master alloy ingot with specified compositions of $Fe_{71}(Nb_{0,8}Zr_{0,2})_6B_{23}$ by induction melting of the pure Fe, Nb, B, Zr elements in argon atmosphere was prepared. First mixture of pure elements in corundum crucible was melted. The master alloy in a quartz crucible with an induction coil and cast into a copper mould by applying an ejection pressure was melted. The plate of bulk metallic material with thickness of 1 mm was obtained.

The X-ray diffraction experiment using a Seifert – FPM XRD 7 diffractometer with Co Kα radiation at 35kV was carried out. The diffraction pattern in range 10 to 100 2θ with step 0.04 2θ and 2s per step was obtained. The observation of microstructure by means of the OLYMPUS model GX71 optical microscope was carried out.

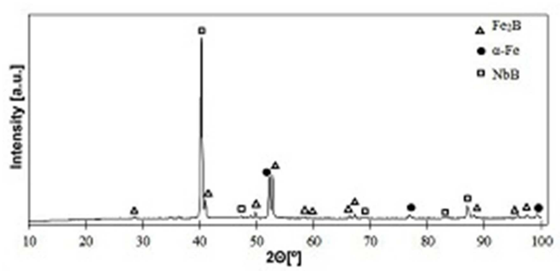

Fig. 1. X-ray diffraction pattern of the $Fe_{71}(Nb_{0,8}Zr_{0,2})_6B_{23}$ alloy plate with thickness of 1mm

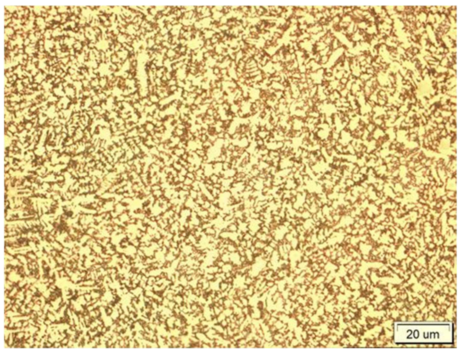

Fig. 2. Image of the microstructure of $Fe_{71}(Nb_{0,8}Zr_{0,2})_6B_{23}$ alloy (magn. 1000x)

The experimental results have been revealed that the $Fe_{71}(Nb_{0,8}Zr_{0,2})_6B_{23}$ alloy can be successfully cast into a plate form. The diffraction record of the $Fe_{71}(Nb_{0,8}Zr_{0,2})_6B_{23}$ alloy plate is shown in Figure 1. The diffraction pattern presents the peaks characteristic for Fe_2B, α-Fe and NbB phases. In tested sample the crystalline phases were created.

Image of the microstructure of tested alloy is presented in Fig. 2. The shape and size of the dendrites indicate formation of crystalline structure.

4. Conclusion

The use of sufficiently large cooling rate of the liquid phase, which is expected to produce a structure characterized by a lack of long range order is the main problem encountered in the preparation of the BMGs.

Furthermore, the melting and casting processes of BMGs should be controlled by the following parameters: the protective atmosphere; the high purity of the initial material, the homogeneity of master alloy and produced samples; the pressure inert gas (Ar); the temperature; the time; the crucible materials and the dimensions of cast samples.

The investigation performed on the sample of tested $Fe_{71}(Nb_{0,8}Zr_{0,2})_6B_{23}$ alloy allowed to formulate the following statements:

- Rapid cooling is the practiced technique which allows the casting of plates with a determine thickness;
- The X-ray analysis and microscopic observation exhibit that the studied Fe-based bulk metallic alloy is crystalline;
- The preparation process of the Fe-Nb-Zr-B alloy requires special technology to provide specific conditions for melting and casting process. Probably, the master alloy hasn't been homogeneous. Separation of the constituent elements significantly has been limited the ability of the glass transition alloy. At the first stage of production, multi-stage casting process or repeated re-melting process to homogenize the chemical composition should be used.

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