Metal Fe-Based Amorphous and Amorphous – Nanocrystalline Materials for Armours Construction[*]

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Abstract. In the present paper, the physical and technical principles of process for production of bulk amorphous alloys are shown. Technical assumptions for construction of experimental unit for melting and casting of new alloys are described. On the basis of the constructional assumptions the laboratory unit for melting and casting of amorphous alloys was made at Product Technology and Application Group in Institute for Ferrous Metallurgy. Fe-based bulk metallic glasses are modern materials of strength properties substantially higher than could be obtained in currently produced steels. Owing to unique combination of high strength, hardness, elasticity, wear and corrosion resistance as well as specific magnetic properties they demonstrate a great potential for application. The paper contains the results of the investigations aimed at development of technology of making parts from Fe-based bulk amorphous alloys which would be deployed in layered passive armours.

Keywords: materials engineering, Fe-based bulk amorphous alloys, nanocrystalline structure, mould suction casting

1. INTRODUCTION

Fe-based bulk amorphous alloys are a new group of materials obtained in the process of cooling from liquid state, omitting crystallization, which leads to

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formation of solid body of disordered arrangement of atoms. Amorphous alloys are characterized with lack of long range order or translational symmetry, which is reflected in change in mechanical properties as compared to crystalline material. These alloys are characterized, depending on the chemical composition with high strength of 3÷4 GPa, hardness of about 8÷13 GPa and specific magnetic properties, high magnetic permeability and low coercivity as well as high corrosion resistance [1-9]. Moreover, amorphous alloys can be used as input material for manufacturing the products having nanocrystalline structure in a manner which would be more effective than methods used at present such as: multidirectional plastic strain or mechanical integration of nanocrystalline powders. At present, Fe-based bulk amorphous alloys are not constructional materials produced in an industrial scale. Bulk amorphous alloys because of their excellent properties, such as: high strength, hardness, elasticity, wear and corrosion resistance, and specific magnetic properties, have a great potential for application in various fields of technology, among others, for components of engines, machining tools, filters, transformer cores, heads, also in medicine (implants, surgical tools) [6]. Recently, information has appeared on attempts to use amorphous alloys in the area of military applications. In the US, under research works financed by Defense Advanced Research Projects Agency (DARPA), at the University of Virginia, non-magnetic Fe-based amorphous alloys contain manganese, molybdenum, as well as carbon-based alloys, of tensile strength of about 3.0 GPa were designed [7]. Shipbuilding industry is interested in one of the versions of alloy, entitled DARVA-Glass101, for the purpose of construction of stealth submarines which do not draw magnetic mines.

A constraints for industrial use of high strength properties of amorphous alloys are significant difficulties in obtaining products of usable dimensions by means of the available and low cost manufacturing technologies. In the case of alloys with the content of Fe above 50%, due to the necessity to ensure cooling rate above $10^5 \div 10^6$°C/s, presently ribbons of thickness up to about 200 μm are manufactured on industrial scale using melt spinning.

The paper presents physical and technical principles of manufacturing bulk amorphous alloys, the construction of the device for melting and casting amorphous alloys, started up at the Product Technology and Application group of the Institute for Ferrous Metallurgy and results of casting tests. It needs to be emphasized that bulk Fe-based bulk amorphous alloys are manufactured on laboratory scale and have not been transferred yet to industry.

2. PHYSICAL PRINCIPLES OF AMORPHOUS ALLOYS MANUFACTURING

Obtaining amorphous alloys is related to three empirical rules derived by Inoue [10]:

- multi-component alloys (consisting more than 3 elements),
- significant difference in atomic size ratios among the three main constituent elements (above 12%),
- negative mixing heats between the main constituent elements.

Satisfying the above rules ensures stability of the undercooled liquid and high glass forming ability – GFA. Another very important parameters defining the capability of alloy to reach amorphous state are: reduced glass transition temperature, critical rate of cooling and size of the cooled area. The reduced temperature of glass transition is defined as:

$$\frac{T_G}{T_m} \tag{1}$$

where: T_G – glass transition temperature, T_m – melting temperature.

In order to increase alloy capability to transit into amorphous state, taking into account the temperature parameters, one should aim at increase in T_G value with simultaneous reduction in the value of T_m parameter as thus as a consequence attempt to achieve the reduced transition temperature aimed at 1. Increase in the value of T_G/T_m results in reduction of the heat that should be transferred from an alloy in a liquid state to reach glass transition temperature. Bulk Metallic Glasses (BMG) are characterized with the value of the reduced transition temperature above 0.6. Critical cooling rate is a crucial parameter determining capability of the alloy for glass transition since reduction thereof results in increase of alloy's glass forming ability. In order to achieve amorphous structure of alloy it should be cooled down from the temperature above T_m at a rate equal or higher than R_C to the T_G temperature. Moreover, this parameter decides on the thickness of the achieved bulk amorphous materials (t_{max}) due to the time required for transferring heat from the entire cross section of the cooled alloy. The value of the critical rate of cooling ranges from 0.10 K/s for the alloy $Pd_{40}Cu_{30}Ni_{10}P_{20}$ a 10^5 K/s for Fe-, Co-, Ni-based alloys. The cooled area (area of the undercooled liquid) defined as:

$$\Delta T_X = T_X - T_G \tag{2}$$

where: ΔT_X – undercooled area, T_X – temperature of crystallization.

Increasing this area results in larger distance of glass transition point from crystallization point which allows to reduce the rate of alloy cooling below crystallization point in comparison with prior cooling rate, which should be applied, when the temperature of the alloy was above *Tx*.

3. MECHANICAL PROPERTIES AND POSSIBLE APPLICATIONS OF AMORPHOUS ALLOYS

Comparison of mechanical properties of bulk amorphous alloys with conventional crystalline materials is presented in Fig. 1 and 2. Table 1 presents the published data concerning mechanical properties of selected amorphous alloys.

Table 1. Mechanical properties of selected amorphous and amorphous-nanocrystalline alloys in room temperature [1-11]

Item	Type of alloy	R_m, GPa	R_e, GPa	A, %	Elasticity of elongation modulus, GPa	Transverse elasticity modulus, GPa	Hardness, GPa
1	$Fe_{80}P_{16}C_3B_1$	2.44	-	-	135.3	-	8.2
2	$Fe_{80}B_{20}$	3.63	-	-	165.7	-	11.0
3	$Fe_{71}Mo_5P_{12}C_{10}B_2$	3.15	2.45	3.6	-	62	8.5
4	$Fe_{64}Cr_3Mo_{10}P_{10}C_{10}B_3$	3.40	2.75	1.2	176	66	9.5
5	$Fe_{65}Cr_2Mo_9P_{10}C_8B_6$	3.55	2.90	3.55	177	67	9.7
6	$Fe_{49}Cr_{15}Mo_{14}C_{13}B_8Er_1$	4.04	3.90	0.10	201	82	-
7	$(Fe_{0,1}Co_{0,1})_{58,5}Cr_6Mo_{14}C_{18}B_3Er_{0,5}$	4.07	3.8	0.35	200	75	-
8	$Co_{43}Fe_{20}Ta_{5,5}B_{31,5}$	5.10	-	1.4	268	-	-
9	$Fe_{44,3}Cr_5Co_5Mo_{12,8}Mn_{11,2}C_{15,8}B_{5,9}Y_{1,5}$	3.0	-	-	257	-	13.0

Bulk amorphous Fe-based alloys, depending on the chemical composition, are characterized with high tensile/compression strength ranging from 2.44 GPa to 4.1 GPa, Young modulus in the range from 135-257 GPa as well as high hardness from 8.2 GPa to 13,0 GPa higher than in the case of crystalline materials. Bulk amorphous alloys containing 48-49 at. % of Fe with addition of Cr, Mo, C, B and Er make it possible to achieve in the case of products of 4÷6 mm diameter the tensile strength of about 4.0 GPa at strain ranging from 0.1 to 0.25 [7].

Alloy of chemical composition $Fe_{44,3}Cr_5Co_5Mo_{12,8}Mn_{11,2}C_{15,8}B_{5,9}Y_{1,5}$ reveals compression strength equal to 3.0 GPa, Young modulus equal to 257 GPa and hardness HV0.2 equal to 13.0 GPa [9]. The best mechanical properties amongst bulk amorphous alloys were gained for Co-based alloy containing Fe, Ta and B [11]. Sample of the said alloy of 2 mm diameter revealed compression strength of 5.1 GPa and Young modulus of 268 GPa.
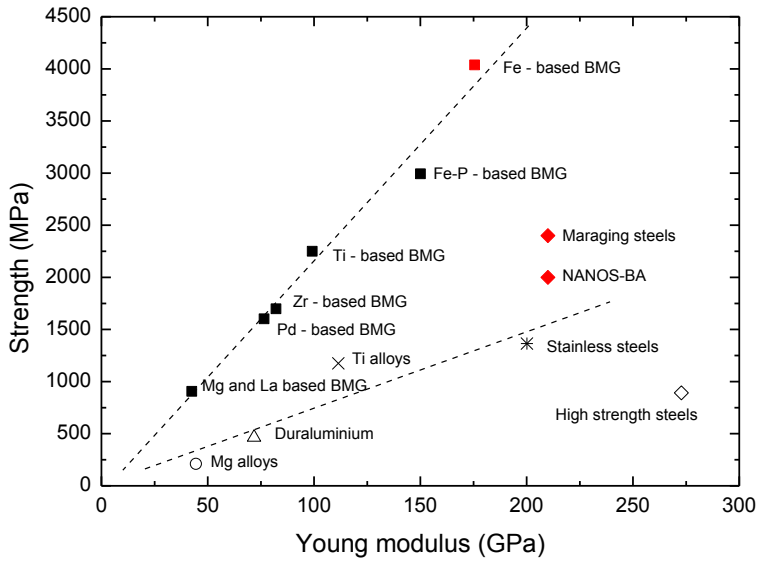
Fig. 1. Tensile strength and Young modulus of amorphous alloys, high strength steels, maraging steel and NANOS-BA steel
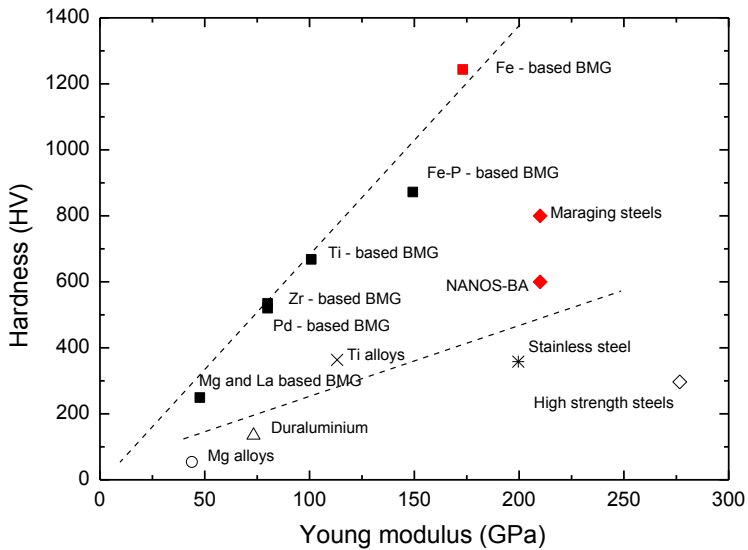

Fig. 2. Hardness and Young modulus of amorphous alloys, high strength steels, maraging steel and NANOS-BA steel

Less advantageous feature of these materials is their low ductility resulting from presence of defects in form of pores and micro-cracks formed during manufacturing process, as well as low work hardening capability [5].

Poor susceptibility for hardening results from the fact that in the case of amorphous structure plastic strain occurs in an non-homogenous manner, i.e. by nucleation and propagation of slip planes. This results in the materials being susceptible to location of deformation and thus uniform elongation is reduced.

4. POSSIBILITIES OF USING AMORPHOUS ALLOYS IN PASSIVE ARMOURS

Development of conventional military technology is effected during continuous rivalry between ammunitions and armours. A reply to development in the range of firing power is improvement in armour protections of vehicles, aircrafts and watercrafts. Since the said vehicles have to retain high mobility, increase in protective effectiveness of armours has to occur without significant increase in their weight. Composite layered armours, consisting of metal layers, laminates, ceramics, which allow to reduce armour weight considerably require attention. The most effective solution amongst armours are the composite armours consisting of several layers of various mechanical properties. Outer ceramic layer takes over the main impact and thermal load from projectile. By disintegration and causing fragmentation of the projectile's core it dissipates considerably projectile's kinetic energy. The remaining energy is absorbed by elastic bottom layer, which may be steel, aluminium or aramid laminates [13, 14].

As compared to ceramics used in construction of armours, mainly on the basis of Al_2O_3 and SiC, amorphous alloys reveal higher susceptibility to plastic strain, from 0.1 to 3.6% (Table 1) and increase in strength properties in the conditions of dynamic strain. For amorphous Zr-based alloys compression strength in the conditions of dynamic strain with a rate of $4000 \ s^{-1}$ is higher by about 45% as compared to strength measured during deformation with a rate of $10^{-2} \ s^{-1}$, Fig. 3 [5]. One should expect that also for amorphous Fe-based alloys their strength will be higher than specified in Table 1.
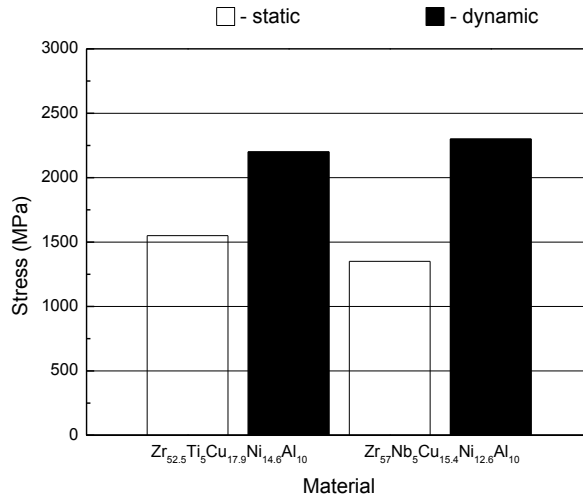
Fig. 3. Comparison of static and dynamic properties of Zr-based amorphous alloys

5. TECHNOLOGIES OF AMORPHOUS ALLOYS MANUFACTURING

Methods manufacturing of amorphous or amorphous – nanocrystalline alloys may be divided into two groups – powder and casting methods – with respect to the form of the final product [15].

The group of "powder methods", similarly to conventional metallurgy, consists of the sequence of technological operations of manufacturing amorphous powders, condensation and agglomeration thereof. "Powder methods" facilitate production of bulk products of any shape and large dimensions. A critical technological operation in "powder methods" is an operation aimed at obtaining amorphous powder of the required chemical composition and desired granulation. The second group gather together set of casting methods where amorphous alloy is manufactured in form of solid product obtained as a result of cooling of liquid alloy by way of contact with the base which is able to fast transfer heat from liquid alloy.

The most popular technology of amorphous products manufacturing is continuous casting of liquid alloys on the surface of rotating wheel. In this manner, ribbons of thickness ranging up to 150 μm, used for transformer cores are manufactured from Fe-based alloys. In order to obtain the product of thicknesses ranging from 1 to 10 mm it is necessary to use alloy of the chemical composition which ensures achievement of low temperature of melting point, so called 'deep eutectics', which allows to obtain amorphous structure at lower cooling rates in the middle of product intersection.

6. TECHNOLOGY AND STRUCTURE OF LABORATORY STAND FOR CASTING OF BULK AMORPHOUS ALLOYS

6.1. Assumptions for the technology of manufacturing products of bulk amorphous alloys

A critical element of the technology in the process of bulk amorphous alloys manufacturing is ensuring high cooling rate which would eliminate or impede crystallization process during solidification. In the technology of manufacturing products in form of castings, cooling rate on the intersection depends on the intensity of heat transfer to the mould and thermal parameters of steel (heat conduction coefficient) which determine heat flow in the castings volume. In this case dimensions and weight of the product are critical factors. The only method of obtaining products of amorphous structure and large dimensions known at present include selection of chemical composition of alloy and preparation of master alloy is to achieve the highest possible susceptibility to glass transition.

Results of research works conducted at the Institute for Ferrous Metallurgy [16, 17] have shown that in order to obtain the amorphous and nanocrystalline steel, a three stage process of alloy preparation for final casting is necessary; the process consists of:

1. Preparation and casting of preliminary alloys in form of two- or three-constituent Fe-based alloys by means of the available technologies used in steel production,
2. Preparation and casting of preliminary alloys on the basis of initial alloys following complementing the chemical composition of steel with alloying elements of lanthanide series, such as Zr, Y and Er and following several remelting in order to homogenize chemical composition,
3. Preparation and casting of final product in form of bars, discs, and/or plates – pressure die casting.

Taking into consideration results of research work [16] the charge for master alloys preparation will be melted by means of induction method in a protective atmosphere of inert gas or in vacuum and that casting will be effected by means of pressure method to copper mould with water-cooled walls.

6.2. Laboratory stand for casting bulk amorphous alloys

Based on the elaborated assumptions the device for melting and casting (line for semi industrial simulation – A3 module) was constructed at the Product Technology and Applications Group at the Institute for Ferrous Metallurgy, which facilitates application of casting method with simultaneous cooling at the rate impeding alloy crystallization.

Views of the stand for melting and pressure die casting of amorphous alloys and moulds for bars and plates casting are presented in Figures 4 as well as 5 and 6.

Fig. 4. Stand for melting and pressure die casting of amorphous alloys
(left and front view)

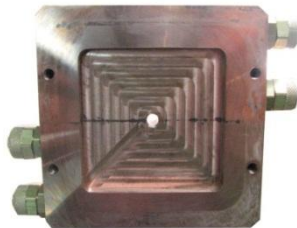Fig. 5. Mould for bar casting of 10 mm diameter and 50 mm length

Fig. 6. Mould for casting of plates 50 × 50 mm, thickness 5 mm

The device is composed of the following devices:

1. Generator supplying power to the section for preparation master alloys and section for remelting and casting,
2. Section for master alloys preparation,
3. Section for remelting and casting composed of:
   a) melting section,
   b) section for transfer of liquid alloy into mould,
   c) mould section.
4. System of control as well as set for measurement and recording of process parameters.

The above device was manufactured by the company ELKON.

7. DESIGNING CHEMICAL COMPOSITION OF BULK FE-BASED AMORPHOUS ALLOYS

Taking into account conditions of amorphous alloys formation and published data concerning mechanical properties achieved for various Fe-based alloys, it was decided that chemical composition of alloy should ensure obtaining the lowest possible eutectic temperature. It was assumed that tests of obtaining bulk amorphous materials or with dominant share of the amorphous phase will be based on Fe and carbon alloys as well as Fe and boron alloys with additions of chromium, molybdenum and/or manganese.

Analysis of phase diagrams using ThermoCalc software [17] has shown that in order to obtain the lowest melting point and low eutectic temperature the ranges of particular alloying elements content in Fe-based alloys should be the following (mass %): 40-60% Fe, 2-4% C, 1-3% B, 20-30% Mo, 3-5% Co, 0-4% Cr, 0-10% Ni, 0-5% Si, 10-25% Mn, 2.5-3,5% Y or 1.5-2.5% Er. It is significant to achieve high contents of carbon and boron, which ensure obtaining alloy of low eutectic temperature. Chemical compositions of alloys presented in Table 2 were selected for casting tests.

The selected compositions are characterized with theoretically high glass forming ability and low melting point. The master alloys were prepared from initial melts obtained from remelting of armco Fe with alloying additives in form of fine elements – Mo, Mn and Cr and pressure die casted. Examples of the photographs of the cast bar and plate are presented in Figures 7 and 8.

Table 2.   Chemical compositions of Fe-based bulk amorphous alloys (mass %)

No of alloy	Fe	Mo	Mn	Cr	Co	C	B	Y	Calculated liquidus temperature, °C (without consideration of Y)
1	50.9	24.3	11.8	4.1	3.8	3.7	1.2	0	1182
2	50.0	23.7	11.4	3.9	3.7	3.6	1.2	2.5	1180
3	54.2	26.1	10.6	4.0	-	3.7	1.2	0	1154
4	52.5	25.3	10.3	3.9	-	3.6	1.2	3.0	1150
5	42.1	15.7	-	15.7	-	3.7	1.8	2.0	1180

Cracks formed in casting process are clearly visible in the pictures.

Fig. 7. Bar of 10 mm diameters cast from master alloy no 2

Fig. 8. Plate of 5 mm thickness cast from master alloy no 2

Due to high brittleness of the casted bars, results of hardness measurements were characterized with considerable spread. The average hardness of alloys no 1 to 4 ranged from 925 HV to 985 HV ±25.4 (9.25 to 9.85 GPa). Results of observations of the microstructure of the obtained castings have shown that at the present stage of works one did not succeed in obtaining large dimension products of amorphous structure by means of pressure die casting. One of the reasons might be heterogeneity of chemical composition on the cross-section and failure to obtain the desired content of yttrium. In the case of alloy no 2, results of x-ray analysis have shown presence of trace quantities of yttrium. ICP analysis has shown that content of yttrium is equal to ca. 0.03 mass %. Formation of cracks in the cast bars and plates results from thermal stresses related to fast heat transfer from bars surface by mould walls, which causes occurrence of considerable temperature gradient on cross section. Thermal stresses in combination with heterogeneity of material are direct reason for material cracking.

Simultaneously with pressure die casting, experiments of centrifugal casting in Philips induction furnace were conducted. Tests of centrifugal casting were performed for alloy no 5 (Table 2). This alloy was casted in form of discs of 40 mm diameter and 1 mm thickness. Discs were cast to the mould of ambient temperature and following mould cooling in liquid nitrogen. In such case, temperature of the mould directly before introduction of liquid alloy was equal to about –130°C and the measured rate of cooling of disc of 1 mm thickness was about 600°C/s. The average hardness of disc was equal to 1200 HV10 (12.0 GPa). Observations of microstructure have shown that in the case of a disc of alloy no 5 cast to the mould cooled in liquid nitrogen it is possible to obtain material of partly amorphous structure. A characteristic feature of the alloy is homogenous area not subject to etching between precipitates of crystallites containing Mo and Y (Fig. 9 and 10).
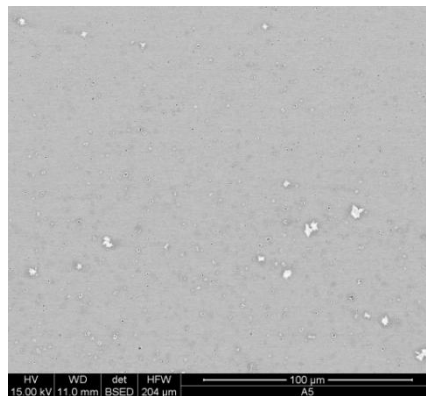

Fig. 9. Structure of disc of 1 mm thickness cast from alloy no 5. Disc was cast to the mould cooled in liquid nitrogen
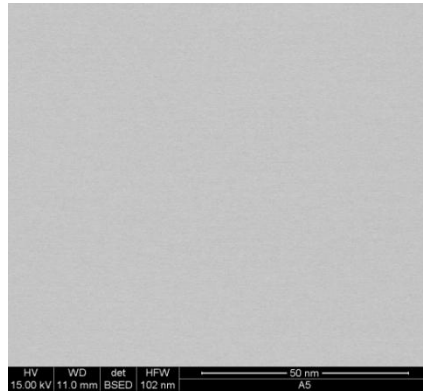
Fig. 10. Structure of the area between precipitates shown in Fig. 10. Disc of 1 mm thickness from alloy no 5 cast to the mould cooled in liquid nitrogen

This fact may indirectly indicate the amorphous structure of matrix between crystalline precipitates.

8. CONCLUSIONS

Bulk amorphous Fe-based alloys are materials characterized with much better strength properties than presently manufactured steels. Depending on the chemical composition these alloys reveal tensile/compression strength – in the range from 2.11 to 4.1 GPa as well as high hardness up to 15.0 GPa (ca. 1500 HV), higher than in the case of crystalline alloys. The highest hardness of steel equal to about 800 HV was observed for maraging steel. Taking into consideration the mechanical properties characterizing amorphous Fe-based alloys one may expect that application thereof in layered structures of passive armours will increasing the protection efficiency and simultaneous reduction in armour weight. The device for melting and pressure die-casting of amorphous alloys enables melting and die casting of amorphous alloys of complex chemical composition and casting these alloys in form of bars of diameter 5 and 10 mm or plates of 5 mm thickness. Such stand facilitates melting and casting in a wide range of parameters such as:

– liquid alloy temperature (up to 2000°C),
– pressure in the main chamber (up to 5 bar),
– negative pressure in the mould (vacuum up to 1 bar),
– intensity of mould cooling (possibility of application of various cooling media).

The achieved results of the conducted tests of melting and casting of bars and plates of maximum dimensions with the designed chemical compositions did not allow to obtain solid castings of amorphous or partly amorphous structure.

Cracking of castings is related to high thermal stresses resulting from considerable temperature gradient between outer surface and core of the casting, heterogeneity of chemical composition and contamination of alloys with non-metallic inclusions. Taking into consideration results of tests of centrifugal casting, which indicate that the designed compositions of alloys allow to obtain bulk alloy of party amorphous structure, it was assumed that further works would be conducted in three directions. The first is aimed at optimization of the process of liquid alloy refining in order to increase glass transition capability owing to elimination of particles being the catalysts of crystallization process. The second direction assumes development of the method of obtaining the products of nanocrystalline structure to be used in layered armours by means of amorphous material heat treatment. The final direction concerns manufacturing plates with nanocrystalline structure of partly- or fully crystallized material, chemical composition designed under the project, with application of powder metallurgy which should facilitate obtaining a product of properties similar to the properties of cast products.

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