Energy and resource saving technologies of formation massive amorphous structures

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Abstract
In the article the results of experimental study of energy-resource saving technologies of formation of massive amorphous structures are resented. Methods of mathematical modeling and optimization of production process of massive amorphous structures, which can cut the time for experimental studies and material resources to create a highly efficient production of amorphous alloys are considered. The results of physical experiments are compared with the results of the calculation.

Received results can be used to analyze the physical regularities and justified choice of technological modes of formation of amorphous structures.
Keywords: RESOURCE SAVING, AMORPHOUS STRUCTURE, CASTING, COOLING MOLD, HEAT CONDUCTION, MATHEMATICAL MODEL, COOLING

1. Introduction

The formation of the amorphous structure of metals and alloys lead to fundamental changes in the magnetic, electrical, mechanical, superconducting and other properties. Amorphous alloys have high toughness, strength, fracture toughness, corrosion resistance, wear resistance. All of the above mentioned properties make amorphous alloys ideal resource saving materials for use in the area of heat power technologies and heat power equipment.

The process of forming of massive layer with an amorphous structure has a number of difficulties, since the cooling of the volumetric array of molten metal, in contrast to the thin layers is a process that is substantially different with the intensity of energy-exchange processes. To obtain the massive amorphous structures we have developed experimental laboratory equipment, where the process of obtaining of massive amorphous structures by casting method in copper cooling mold with fast cooling was investigated .

2. Theoretical

To obtain the amorphous structure in pure metals melt, cooling rate should not be lower than 10^6 K / s, which is difficult to achieve for a given technology.

Alloys with additives, which increase the tendency of the liquid melt to the volumetric amorphization were chosen as experimental. Alloys $Cu_{45}Ti_{35}Zr_{20}$, $Ni_{62,4}Nb_{37,6}$, $Fe_{80}P_{13}C_7$, $Co_{75}Si_{15}B_{10}$ were made of the powder components. To prepare the alloys, pure charge materials were used. The investigated alloys were melted in an induction high-frequency furnace in atmosphere of argon by direct melting of components method. The smelt is poured into cooled copper mold through a hole in the bottom of the crucible after obtaining a homogeneous smelt. Chemical composition of main components of the alloy was controlled by micro-X-ray analysis up to ± 1 at% and local ~ 1,0 microns.

The process for obtaining of massive metal layer with an amorphous structure was carried out by casting in the water-cooled form, during active heat removal heat will be expended for the evaporation of water, which is near the contact surface, in such case three cooling modes can be considered [1-3].

In the first case water velocity has small values and during cooling the vapor layer is formed enveloping heat-conducting surface. In this case, the surface on the water side is covered by steam, creating a thermal resistance to heat flow.

In the second case, increasing the velocity of the cooling water, vapor phase at heat exchange surface will be exposed to destruction, which leads to an increase in the intensity of the heat sink.

In the third case, during turbulent flow a water mass flow rate has maximum value and the percentage of the vapor phase will have minimum, the water will push the vapor and the cooling rate in this case will be maximum.

Therefore, changing the water flow rate in the equipment, the speed of the cooling water in the heat exchange wall increases gradually, heat flow density on the cooled outer surface of the mold and of solidification process consequently can be controlled.

Solidification of the ingot occurs as a result of heat removal of superheat of liquid metal and latent heat of solidification from the melt into the cooled form and further in the environment [4,5].

For structure investigation and determination the degree of amorphization there were cut several samples (templates) in such a way to determine changes in the structure according to the number of cross sections. To reveal the microstructure chemical etching using a reagent consisting CH_3 COOH, HNO_3 and HF was performed. To determine the degree of amorphization electron-macroscopic research in the mode of direct expansion was conducted. For visual examination microsections and photographing used the microscope MMP-4 [6].

Metallo-physical studies determined that the analyzed metal layer obtained by casting in cooled form in the first case Figure 1 has a crystalline ferrite-pearlite structure, formation of the amorphous structure did not happen, since the velocity of the cooling water has a value less than 1 m/s, at maximum water temperature of 15 °C and the maximum thickness of the metal layer.

The investigated layer of metal in the second case fig.2 partly has an amorphous structure on the boundaries layer near the boundary with the cooling medium, and in the middle of microcrystalline ferrite-pearlite structure, besides ferrite and perlite are present as martensite, bainite and residual austenite. The formation of the amorphous structure at the layer boundaries due to an increase of the velocity of the cooling water up to 2 m/s and decreasing the temperature of water up to 7 °C with average values of metal layer thickness.

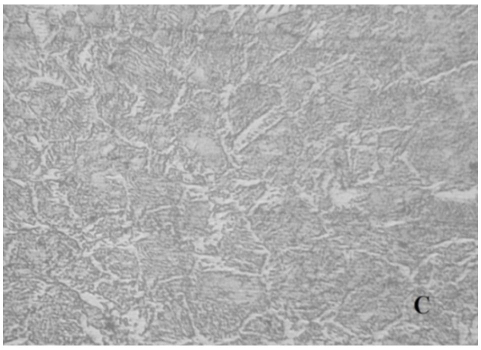
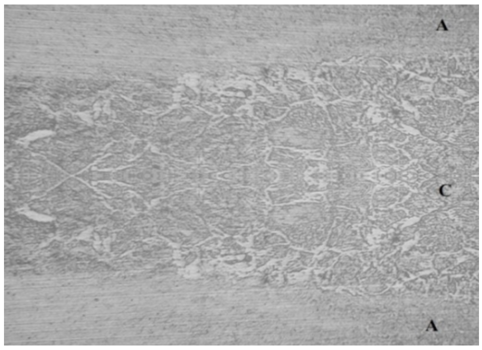


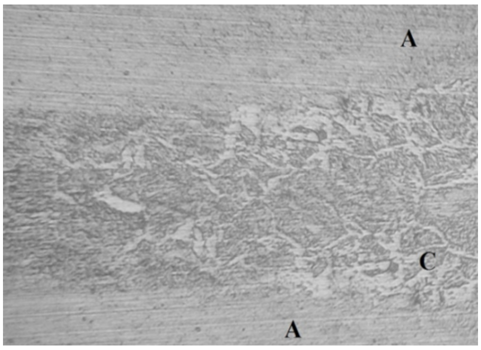
Figure 1. The crystalline structure of massive layer of metal



A – amorphous structure, K - the crystalline

Figure 2. Amorphous-crystalline structure of massive layer of metal

In the third case in figure 3 for turbulent flow conditions investigated layer of metal has a partially amorphous structure on the boundaries layer near the boundary with the cooling medium, and in the middle layer of microcrystalline ferrite-pearlite structure obtained at the maximum velocity of water of 3 m/s, the minimum temperature of water 5 °C and the thickness of metal layer 5 mm. Since the cooling rate in this case will have a maximum value, there observed an increase of the amorphous metal phase.



A – amorphous structure, K - the crystalline

Figure 3. Amorphous-crystalline structure of massive layer of metal, obtained at high cooling rate

Based on the results of experimental researches, formation of massive layer with an amorphous structure can be achieved at the minimum values of cooling water temperature and the maximum speed of the cooling water, but the main factor is the value of the thickness of metal layer.

Thermal stability of amorphous alloys and the solidification process was studied by differential scanning calorimeter Setaram DSC 131. For processing of thermograms there was used software package included in the calorimeter set. Processing of experimental data was carried out in the software package for statistical analysis StatSoft Statistica 6.0 figure 4.

The maximum degree of cooling is achieved at the surfaces of the layer adjoined to the cooled walls of the mold, at the maximum velocity of the cooling water in heat exchange wall forms and a minimum temperature of the cooling water (figure 4), but the main factor that has the greatest impact on the degree of amorphization is the thickness of the melt. The crystallization temperature inside the layer is higher than of the surface layer. The duration of the cooling process inside the layer is 5-10 times higher [7,8].

Metallo-physical research recorded that some "amorphous" phases located inside the layer consist of microcrystals, which in its turn proves pseudo-amorphous of these phases.

Experimental investigations of casting technology in cooled form require time- and material resources, where to reduce some of them allows the usage of methods of mathematical modeling and optimization.

Using modern methods and means of mathematical modeling, we can solve complex problems of heat transfer, as well as to investigate the features of the technological process, identify the qualitative picture of the interaction of various factors. It is possible to establish quantitative functional dependencies by means of calculation [2].

The mathematical formulation of the problem of metal casting in cooled form includes heat conduction equation describing the thermal phenomena at the relevant boundary conditions. The first step begins with setting of type and dimensions of the model (1D, 2D, or 3D) [3].

When considering the joint solution of the model of overall heat transfer and model of weakly compressible liquid of Navier-Stokes equations in the start menu, one should select the 2D task (General heat transfer) and 2D task (Weakly Compressible

Navier-Stokes). Built on such algorithm model of the process of metal casting in the cooled form of a graphical solution, where we can see the temperature distribution (temperature field), direction of the current lines and temperature gradient.

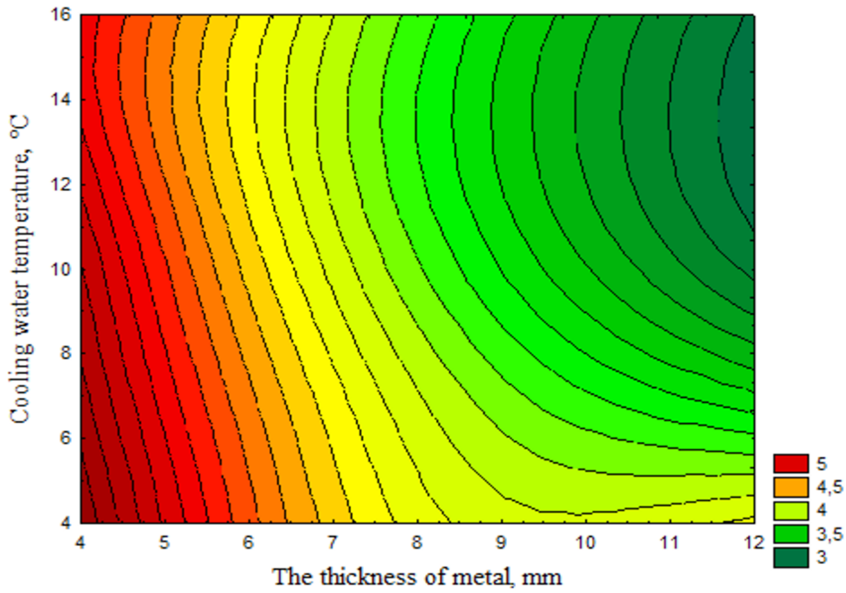


Figure 4. Dependence graph of the degree of amorphization on the cooling water temperature and thickness of metal layer

Thus, the temperature distribution in the solidifying ingot is determined by solving the system of equations (1) - (2) with appropriate boundary conditions [3].

To solve these equations it is necessary to formulate initial and boundary conditions, ie, temperature distribution at the initial time and conditions of heat exchange with the environment.

Necessary condition for solving the equations is the knowledge of thermophysical properties of metals and alloys at high temperatures: heat capacity, thermal conductivity and heat of solidification (glass transition).

$$\rho \tilde{N}_{\rho} \frac{\partial T}{\partial t} + \nabla(-k\nabla T) = Q + q_s T \qquad (1)$$

where: q_s [W/m³·K] is absorption coefficient, Q [W/m³] is heat source, k [W/m·K] is coefficient of thermal conductivity, T [K] is temperature, ρ [kg/m³] is density, C_p [J/kg·K] is heat capacity at constant pressure, ∇ - Nabla Operator.

Navier-Stokes equation

$$\rho \frac{\partial u}{\partial t} + \rho(u\nabla)u = \nabla\left[-pI + \mu\left(\nabla u + (\nabla u)^T\right) - \frac{2}{3}\mu(\nabla u)I\right] + F$$

$$\frac{\partial \rho}{\partial t} + \nabla(\rho u) = 0$$

where: ρ [kg/m³] is density, η [P·s] is dynamic viscosity, k_{dv} [P·s] is volume viscosity, u [m/s] is velocity.

As a model alloy there was selected alloy having a good tendency to amorphization due to the content of alloy of elements prone to amorphization, such as zirconium Zr.

From previous studies it is known that the thickness of the melt during formation of amorphous structure has a significant impact on the structure and properties of metals and alloys. Accordingly, as a study, we chose two cooled molds with different dimensions, which in its turn determined the thickness of the melt, and the possibility of obtaining an amorphous structure. In table 1 there presented thermophysical properties of investigated alloy.

Alloy $Cu_{45}Ti_{35}Zr_{20}$ is characterized by a high hardness, strength and thermal stability as compared with other massive amorphous alloys. When Zr content increases up to 18%, thermal stability of the alloy also increases from 690 K to 815 K, which substantially increases the area of application this type of alloys.

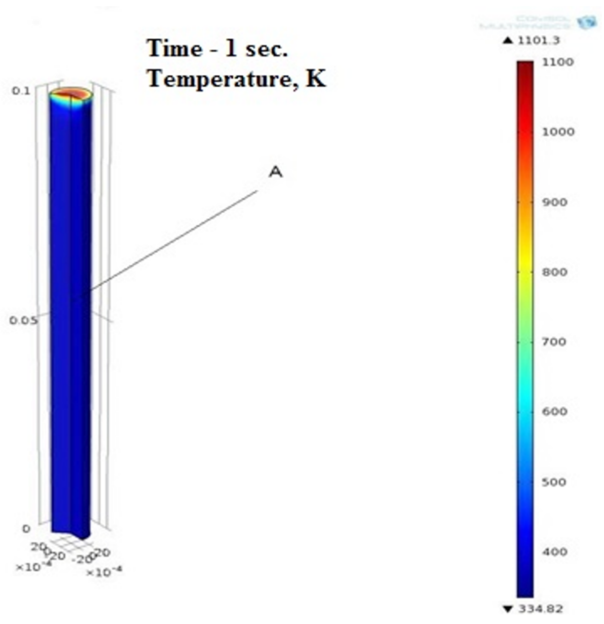
Table 1. Thermophysical properties of investigated alloy

Alloy	Melting temperature, K	Temperature of transition to the amorphous state, K	Alloy density, kg/m³	Heat capacity of the alloy, J/(kg·K)	Coefficient of thermal conductivity, W/m·K
$Cu_{45}Ti_{35}Zr_{20}$	1063	683	6900	385	340

The formation of the amorphous structure of this alloy is quite ambiguous process. The conditions for the solution of thermal problem of alloy casting $Cu_{45}Ti_{35}Zr_{20}$ are shown in Table 2. The results of modeling are shown in figures 5-8 in graphs and fields of temperature distribution. Graphs provide an effective estimation of the intensity of heat transfer during the casting process, which makes it possible to estimate and predict the ability of alloys to the amorphization of the structure.

Table 2. The parameters for solving of thermal problem of alloy $Cu_{45}Ti_{35}Zr_{20}$ casting

Parameter	Parameter value
Temperature of melt before the casting process	T_in = 1063 K
Temperature at the walls of cooled mold	T_к = 373 K
Casting speed	v_cast = 1,6 mm/s
Smelt density	ρ=6900 kg/m³
Specific heat of the metal	Cρ= 385 J/(kg·K)
Dynamic viscosity	η=0,0434 P·s
Latent heat	dH=205 kJ/kg
Coefficient of thermal conductivity	k=340 W/m·K
Measurement interval of casting process	0-1 s
Size of the form (casting thickness): height × diameter mm	100×3, 100×10



A – amorphous structure

Figure 5. Temperature field of the melt $Cu_{45}Ti_{35}Zr_{20}$ in a cooled form

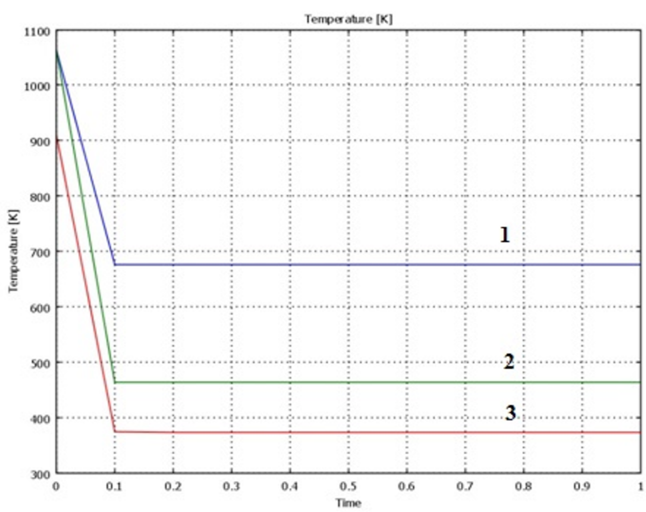
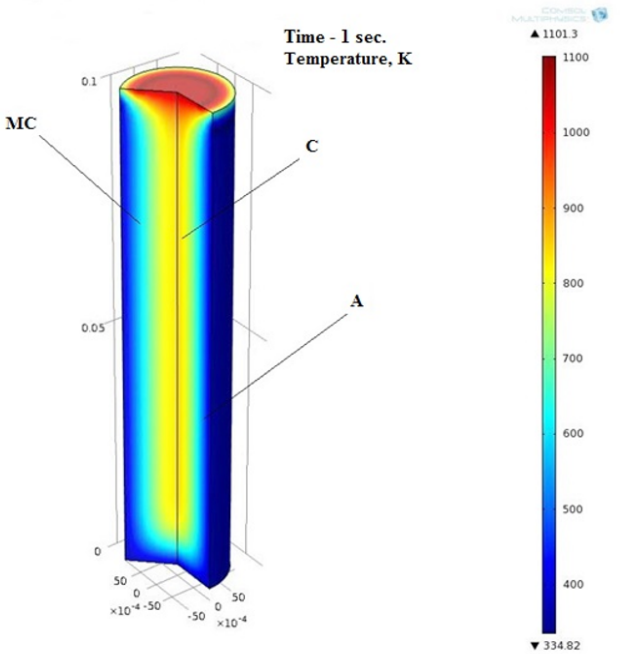


Figure 6. The temperature distribution in the alloy $Cu_{45}Ti_{35}Zr_{20}$ at a temperature of the mold wall 373 K
1 – casting center, 2 – near the cooled walls of the mold, 3 - near the boundary with the cooling medium.



A – amorphous structure, MC – micro crystalline, C - crystalline

Figure 7. Temperature field of the melt $Cu_{45}Ti_{35}Zr_{20}$ in a cooled form

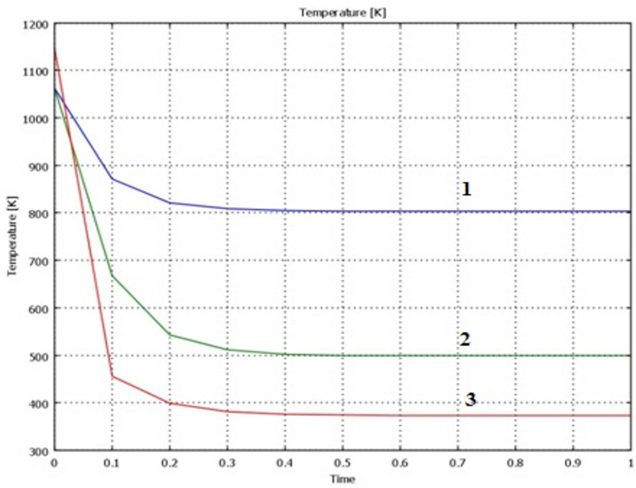


Figure 8. Temperature distribution in the alloy

$Cu_{45}Ti_{35}Zr_{20}$ at a temperature of the mold wall 373 K
1 – casting center, 2 – near the cooled walls of the mold,
3 - near the boundary with the cooling medium.

From these graphs 5-6 one may see that in the range of 1 second, ultra-fast cooling of the metal takes place. It can be concluded that the formation of the amorphous structure (A) (figure 5) around the metal layer is possible only with maximum cooling rate on the walls of a cooled mold fig.6. The other graphs 7-8 show that with the decrease of cooling rate there occurs only partial amorphization of near-cooled walls of the mold, which leads to formation of both the amorphous (A) and the crystalline (C) structures (fig. 2-3). Closer to the center of the ingot in result of less heat transfer there formed microcrystalline (MC) metal structure. In the central part of the ingot even at the maximum degree of cooling the formation of amorphous structure does not occur. The presence of convective flows in the middle of the ingot leads to increase of heat transfer and increase of cooling rate, in consequence of which it is possible to achieve microcrystalline metal structure with improved mechanical properties.

For alloy $Cu_{45}Ti_{35}Zr_{20}$ critical cooling rate was 10^2-10^3 K / sec which made it possible to obtain samples with an amorphous structure, as proved by metallo-physical, X-ray diffraction studies. Formed hardening amorphous-crystalline structures have good mechanical properties, the hardness of the alloy is 750 HV.

3. Conclusions

The maximum degree of cooling during casting of metal into the cooled form is achieved in the surfaces layer adjacent to the cooled walls of the mold. The crystallization temperature inside the layer is higher than the surface layer. The duration of the cooling process inside the layer is 5-10 times greater.

The experimental and calculated data showed that when using casting method into cooled mold to obtain amorphous products with the thick of several millimeters, it is required to use alloys with sufficiently low critical cooling rate of less than 1000 K/s. Obtaining massive amorphous castings is possible when the thickness of a few millimeters when using this experimental casting method.

There determined two main factors that limit the thickness of the amorphous products: 1. Reduction of heat transfer coefficient from the melt to the forms with increasing of thickness of the product and local melt crystallization, which depends on the volume of the molded product and increases with the thickness of the product near to critical value.

Massive amorphous alloys of copper-titanium-zirconium system represent the greatest interest of investigated alloys. From other massive amorphous alloys they differ by high hardness, strength and thermal stability. When Zr content increases up to 18%, the thermal stability of the alloy increases as well from 690K to 815 K, which substantially increases the area of application of this type of alloys.

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Efficiency evaluation of thermal insulation use in cryolithic zone mine openings

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