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ENERGY AND RESOURCE SAVING TECHNOLOGIES OF FORMATION OF MASSIVE AMORPHOUS STRUCTURE

Abstract

The article presents the results of an experimental study of energy-resource saving technologies of formation of massive amorphous structure. Considered are the methods of mathematical modeling and optimization of process production of massive amorphous structures, which can reduce experimental studies and material resources to create a highly efficient production of amorphous alloys. 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, cooled form, 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, and other superconducting properties. Amorphous alloys have high toughness, strength, fracture toughness, corrosion resistance, wear resistance. All of the above 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 massive layer with an amorphous structure has a number of difficulties, since the cooling of the volumetric array molten metal, in contrast to the thin layers is a process that is substantially different in intensity of energy-exchange processes. For obtaining massive amorphous structures we have developed experimental laboratory equipment, which investigated the process of obtaining massive amorphous structures by method of casting in copper cooled form with fast cooling.

2. Theory

For the possibility obtaining of the amorphous structure in pure metals melt cooling rate should not be below 10^6 K/s, which is difficult to achieve for a given technology.

The investigated alloys were selected with additives which increase the tendency of the liquid melt to the volumetric amorphization. Alloys $Cu_{45}Ti_{35}Zr_{20}$, $Ni_{62,4}Nb_{37,6}$, $Fe_{80}P_{13}C_7$, $Co_{75}Si_{15}B_{10}$ which 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 method of direct melting components. After obtaining a homogeneous melt through a hole in the bottom of the crucible the melt is poured into cooled copper mold. The chemical composition of the main components of the alloy was controlled by micro-X-ray analysis up to ±1% and local ~1.0 microns.

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

In the first case water velocity and has small values in the process 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 in the vapor phase the heat exchange surface will be exposed to destruction, which leads to an increase in the intensity of the heat sink.

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

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

Solidification of the melt occurs as a result of heat removal superheat of liquid metal and latent heat of solidification from the melt into the cooled form and further in the environment [1].

For structure investigation and determining the degree of amorphization was excised several samples (of templates) so as to be able to determine changes in the structure on a number of cross sections. To reveal the microstructure chemical etching was performed by using a reagent consisting of CH_3 COOH, HNO_3 and HF. To determine the degree of amorphization conducted electron-macroscopic research in the mode of direct expansion. Visual examination microsections and photographing used the microscope MMP-4 [1].

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

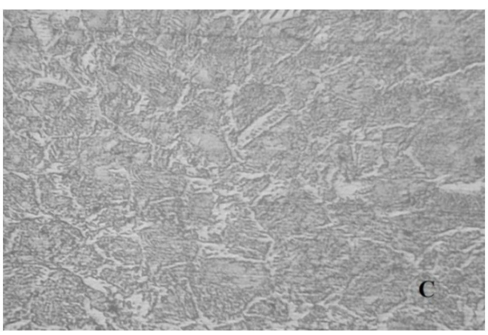

Fig. 1. The crystalline structure massive layer of metal

The investigated layer of metal in the second case in Figure 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 in the velocity of the cooling water to 2 m/s and decreasing the temperature of water to 7°C with average values of metal layer thickness.

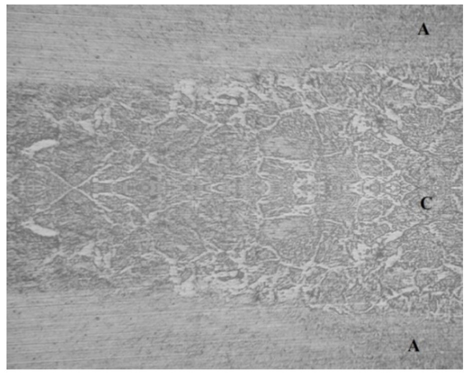

Fig. 2. Amorphous-crystalline structure a massive layer of metal: A – amorphous structure, C – the crystalline

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 resulting at the maximum velocity of water of 3 m/s, the minimum temperature of the water 5°C and the thickness layer of metal is 5 mm. Since the cooling rate in this case will have a maximum value observed an increase of the amorphous metal phase.

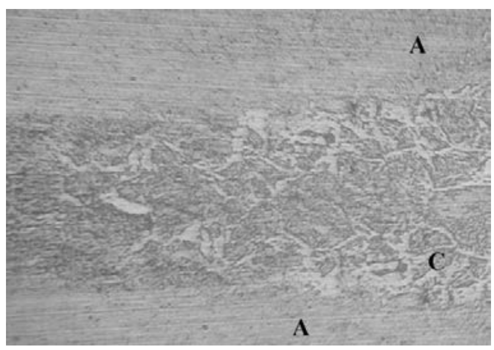

Fig. 3. Amorphous-crystalline structure a massive layer of metal, obtained at high cooling rate: A – amorphous structure, C – the crystalline

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

Thermal stability of amorphous alloys and the solidification process was studied by differential scanning calorimeter Setaram DSC 131. For processing of thermograms using the software package included in the kit calorimeter. 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 adjacent 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 (Fig. 4), but the main factor that has the greatest impact on the degree of amorphization serves the thickness of the melt. 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 more [2].

Metallo-physical research, it was found that some "amorphous" phase located inside the layer composed of microcrystals, which in turn proves these pseudo-amorphous phases.

Experimental investigations technology of casting in cooled form is time- and material resources, which allows you to reduce the use 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 by means of calculation to establish quantitative functional dependencies [2].

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

When considering the joint solutions model the overall heat transfer and model of weakly compressible liquid Navier-Stokes equations in the start menu, select the 2D problem (General heat transfer) and 2D problem (Weakly Compressible Navier-Stokes). Built on such algorithm model of the process of casting metal in the cooled form of a graphical solution, which we can see the temperature distribution (temperature field), the direction of the flow lines, a temperature gradient.

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

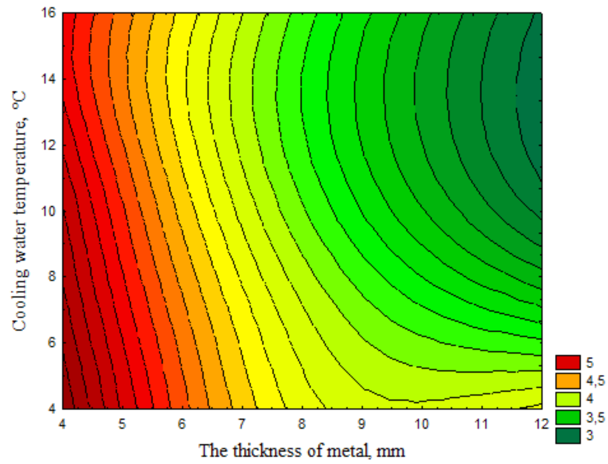

Fig. 4. Graph of the degree of amorphization of the cooling water temperature and the thickness of layer of metal

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

A 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).

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

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, ∇ – Operator Nabla.

Navier-Stokes equations

$$\rho \frac{\partial u}{\partial t} + \rho(u\nabla)u =$$
$$= \nabla\left[-pI + \mu\left(\nabla u + (\nabla u)^T\right) - \frac{2}{3}\mu(\nabla u)I\right] + \qquad (2)$$
$$+F\frac{\partial \rho}{\partial t} + \nabla(\rho u) = 0$$

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

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

Table 1. Thermophysical properties of the investigated alloy

Alloy	The melting temperature, K	The temperature of transition to the amorphous state, K	The density of the alloy, kg/m³	The 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

Alloy $Cu_{45}Ti_{35}Zr_{20}$ from other massive amorphous alloy characterized by a high hardness, strength and thermal stability. When content increases Zr to 18% increases the thermal stability of the alloy from 690K to 815 K, which substantially increases the area of application of this type of alloys. The formation of the amorphous structure of this alloy is quite ambiguous process. The conditions for the solution of thermal problem casting alloy $Cu_{45}Ti_{35}Zr_{20}$ shown in Table 2. The results of modeling in graphs and fields of temperature distribution are shown in Figures 5-8. Graphs provide an effective estimate 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 thermal problem of casting alloy $Cu_{45}Ti_{35}Zr_{20}$

The parameter	The parameter value
Temperature of the melt before the casting process	T_in = 1063 K
The temperature at the walls of a cooled mold	T_к = 373 K
Casting speed	v_cast = 1.6 mm/s
The melt density	ρ = 6900 kg/m³
The specific heat of the metal	Cp = 385 J/(kg·K)
The dynamic viscosity	η = 0.0434 P·s
The latent heat	dH = 205 kJ/kg
Coefficient of thermal conductivity	k = 340 W/m·K
The measurement interval of the casting process	0-1 s
The size of the form (casting thickness): height × diameter mm	100 × 3, 100 × 10

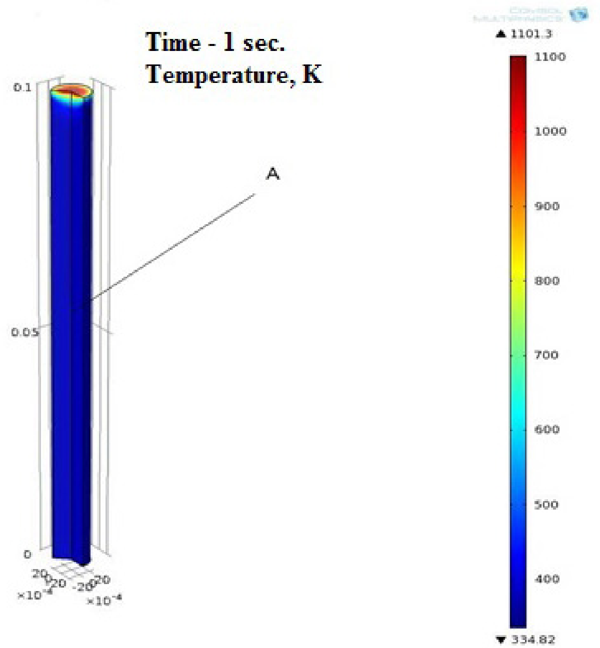

Fig. 5. The temperature field of the melt $Cu_{45}Ti_{35}Zr_{20}$ in a cooled form: A – amorphous structure

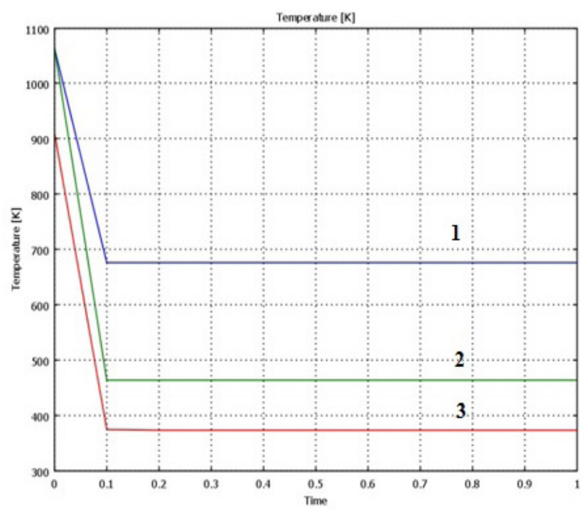

Fig. 6. The temperature distribution in the alloy $Cu_{45}Ti_{35}Zr_{20}$ at a temperature of the mold wall 373 K
1 – casting center, 2 – near the cooled walls of the mold, 3 – near the boundary with the cooling medium

From these graphs Figure 5-6 shows that in the range of 1 second, ultra-fast cooling of the metal. It can be concluded that the formation of the amorphous structure (A) (Fig. 5) around the metal layer is only possible with the maximum cooling rate on the walls of a cooled mold – Figure 6. The other Figures 7-8 show that with decreasing cooling rate occurs only partial amorphization of near-cooled walls of the mold, which leads to formation of both the amorphous (A) and the crystalline (C) of the structure (Fig. 2-3).

environment

Closer to the center of the layer as a result less of heat transfer is formed microcrystalline (MC) of the metal structure. In the central part of the layer even at the maximum degree of cooling the formation of amorphous structure does not occur. The presence of convective flows in the middle layer leads to an increase heat transfer and increase the rate of cooling can be achieved there by microcrystalline metal structure with improved mechanical properties.

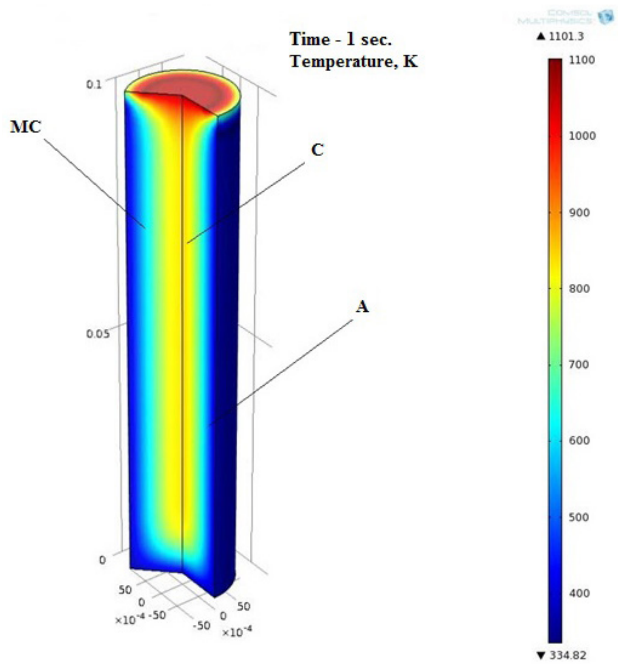

Fig. 7. The temperature field of the melt $Cu_{45}Ti_{35}Zr_{20}$ in a cooled form: A – amorphous structure, MC – fine crystalline, C – the crystalline

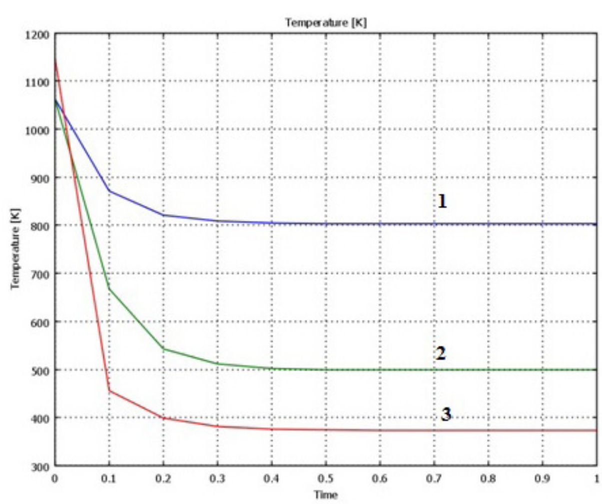

Fig. 8. The temperature distribution in the alloy $Cu_{45}Ti_{35}Zr_{20}$ at a temperature of the mold wall 373 K 1 – casting center, 2 – near the cooled walls of the mold, 3 – near the boundary with the cooling medium

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 evidenced by metallo-physical, X-ray diffraction studies. Obtained when hardening amorphous-crystalline structures have good mechanical properties, the hardness of the alloy is 750 HV.

3. Conclusions

The maximum degree of cooling during the molding process of the metal to 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 to cooled mold to obtain amorphous products thick several millimeters required alloys with sufficiently low critical cooling rate of less than 1000 K/s. Obtaining massive amorphous layer is possible when the thickness of a few millimeters when using this experimental casting method.

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

The greatest interest of investigated alloys represents massive amorphous alloys of copper-titanium-zirconium. From other massive amorphous alloys they are characterized by high hardness, strength and thermal stability. When content increases Zr to 18% increases the thermal stability of the alloy from 690K to 815 K, which substantially increases the area of application this type of alloys.

References

[1] Pavlenko A.M., Usenko B.O., Koshlak H.V.: *Analysis of thermal peculiarities of alloying with special properties*, Metallurgical and Mining Industry, 2 (2014), pp. 15-20.

[2] Pavlenko A.M., Usenko B.O., Koshlak H.V.: *Research the energyefficient process of high-speed casting of metal between the cooling rolls*, Metallurgical and Mining Industry, 5 (2014), pp. 68-72.

[3] Pavlenko A.M., Usenko B.O., Koshlak H.V.: *Mathematical modeling of the casting process in Comsol 3.5a package*, Metallurgical and Mining Industry, 1 (2015), pp. 132-140.