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Production feature of soft magnetic amorphous alloys

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Abstract. Methods for making nanocrystalline alloys have been discussed. Temperature dependences of the surface tension (σ), electric resistivity (ρ), magnetic susceptibility (χ) and kinematic viscosity (ν) have been obtained. Comparison of the properties of amorphous ribbons obtained by the pilot and serial technologies has been conducted. Science-based technology of multi-component alloy smelting makes it possible to prepare equilibrium smelt, the structure of which has a significant effect on the properties of the amorphous ribbon before spinning and kinetics of its crystallization has been offered.

Introduction. Soft magnetic iron-nickel, iron-cobalt, iron-chromium and other high alloys have special physical and physicochemical characteristics. They are determined not only by an exact chemical composition, but also by factors of their production. Normal magnetic properties corresponding to the normative and technical documentation can be achieved by smelting in open furnaces. To obtain alloys with better and high magnetic properties vacuum units and smelting processes are used [1-4].

Distinctive features of soft magnetic alloys are their high magnetic permeability, low coercive force, ability to be treated by plastic deformation, and higher specific electrical resistivity.

Such indicators are achieved by adding nickel, cobalt, chromium, manganese, molybdenum, silicon and other elements to the alloys composition. Along with smelting processes hard metal heat treatment is very important [5]. However, structural features of steels and alloys which above all are determined by the selectivity of hardening phases and accompanied by the segregation of elements have a considerable influence on the properties of metal products.

Main part. The production of nanocrystalline materials with particle size from 1 to 10 nm and soft magnetic amorphous alloys improved special characteristics of products considerably.

The easiest method to obtain nanocrystalline powders is to evaporate material at a controlled temperature either under inert gas with subsequent condensation of steam or in the reaction zone with the formation of spherical particles, or on surfaces, where particles have faceting.

A plasma-chemical method of obtaining nanopowders is the most common chemical methods among others. The reaction is carried out in non-equilibrium conditions providing for a high rate of nucleus formation of the new phase and a low speed of their growth.

A nanoparticle deposition in colloidal solutions involves the consistent implementation of the following operations: a synthesis of starting reagents of the solution and a reaction termination at a particular point in time, after which the disperse system changes from a liquid colloidal state into a dispersed solid one. The method has high selectivity and allows producing particles with a very narrow size distribution.

Quite an effective way of obtaining nanocrystalline powders is mechanical abrasion. During the process of the metal synthesis grinding and plastic deformation of substances take place, the mass transfer is accelerated, as well as mixing of mixture components is performed at an atomic level, and chemical interaction of solid reagents is activated.

The way of obtaining nanopowders by the controlled crystallization of the quenched amorphous state is structurally simple and the most common. The amorphous structure is formed during fast (speed $\geq 10^6$ deg/sec.) cooling of the smelt. A jet of liquid metal with a certain speed is sent to the surface of a fast-rotating cylinder (or a disk), made of a material with high thermal conductivity (such as copper).

The structure of nanocrystalline alloy is a two phase system, in which one of the phases is nanocrystals, and the other one is a remaining amorphous matrix. Nanoalloy properties depend on composition, size and number of nanocrystals, as well as their relationship to the amorphous phase. The main advantage of such materials over crystalline ones is a favorable combination of low coercive force H_c and high relative magnetic permeability μ_{max}. Besides such main components as iron, nickel, cobalt nanoalloys consist of amorphizing elements such as boron, silicon, phosphorus, and others, which lower amorphization temperature t_a to the balance $t_a/t_L = 0.45$, and alloying components involved in the formation of special physical properties and performance characteristics of the finished product.

It is known that equilibrium metallic liquid is an analogue to a metastable amorphous state. Results of studies conducted by different authors (see, in particular, [1-4, 6,7] prove that there are nano-sized clusters or local microassotiations in the structure of these materials, which shall have the same meaning for the theory of amorphous and liquid states as an elementary cell for the theory of crystals [8]. According to the authors [9-11] a local order means that a geometric shape of a cluster is close to the FCC- and HCP- lattices and stable in time, i.e. the time of their life significantly exceeds the period of atom oscillations.

Molten metals and alloys are condensed substance, special state of which is caused by a lack of clear cluster boundaries, distortion of translational symmetry and a dynamically excited state of atoms located in an outer nuclear layer of a cluster, energetically strong interaction of atoms within the cluster, which helps to increase the electron density at the Fermi level [1].

The proportion of foreign atoms in the cluster, evaluated using experimental data, is about 15%. The role of such atoms for the formation of the properties of materials becomes even more significant, given that they have a different electronic configuration due to the change of valence and a decrease of electron density. This leads to weakening of the interatomic interaction with other atoms of the cluster and a significant increase in an amplitude of oscillations.

Another important aspect of the metal smelts structure is their non-equilibrium and heterogeneity depending not only on the composition, but also on the alloyage conditions of components. The non-equilibrium is stipulated by an uneven distribution of atoms among clusters, and the heterogeneity is stipulated by an uneven distribution of clusters differing in structure within the nanovolume of the matter.

The speed at which the equilibrium is reached is significantly less than the alteration intensity of the external environmental changes in multi-component metallic smelts. This results in the prolonged retention of the non-equilibrium states. Therefore, liquid smelts of the identical composition, in the same conditions, can be distinguished by short-range order parameters, the nature of inter-particle interactions and the way of elements distribution . This influences on the course of such processes as diffusion, crystallization and then phase transformations and distribution of atoms in cast and deformed metal [1]. Numerous experimental studies revealed the following pattern: the higher the degree of the smelt equilibrium is before solidification, the better the quality parameters of the hard metal are [1-4].

Under production conditions the equilibrium state of the smelt or a state related to it is achieved most effectively in the course of temperature-time treatment of liquid metal during smelting. Modes of

such technology are developed on the basis of data on structure-sensitive properties of smelts and solid metal quality indicators [1, 3-4].

Let us consider the influence of the smelting technology with temperature-time processing of the smelt (TTP) using some parameters of the structure and properties of the alloy $Fe_{82}B_{12}Si_4C_2$ in liquid and amorphous states. In Figure 1 you can see temperature dependences of the surface tension (σ), electric resistivity (ρ), magnetic susceptibility (χ) and kinematic viscosity (ν), which show that when heated to a certain critical temperature (t_c) polytherms of heating and cooling do not match. Hysteresis represents significant structural changes taking place in the smelt at $t_{heat} \geq t_c$.

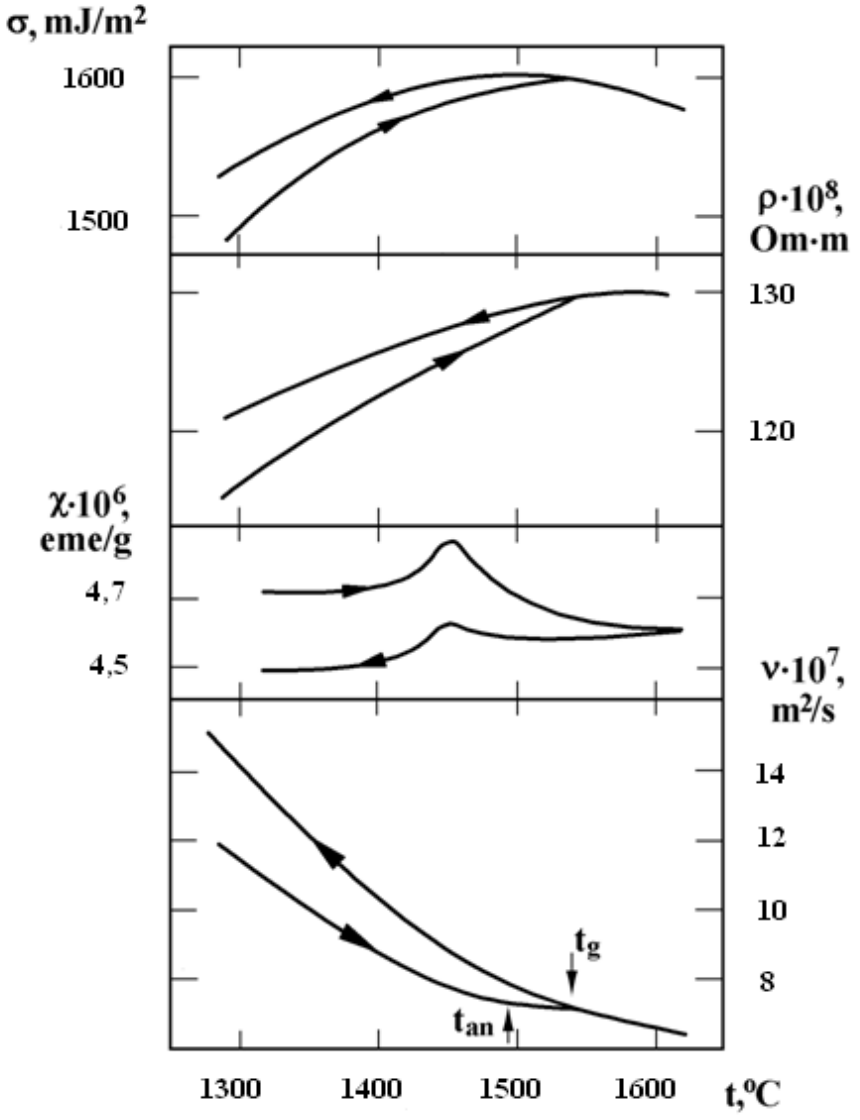

Figure1. Temperature dependences of the surface tension (σ), electric resistivity (ρ), magnetic susceptibility (χ) and kinematic viscosity (ν) of liquid $Fe_{82}B_{12}Si_4C_2$ alloy during heating and cooling

The most informative parameter for iron-based alloys is kinematic viscosity. At the temperature around 1500 °C the exponential dependence of ν(t) degenerates into a linear one, and in the interval t_{an} - t_g the thermal coefficient dν/dt is virtually zero, and for some alloys becomes positive.

The structural state of multi-component alloys is quite difficult to achieve because of the strong chemical interaction of heterogeneous atoms. The studied composition is defined by the formation of borides, silicides and carbides of different types, each of which potentially has the ability to form clusters. Therefore, in multicomponent fluids at the same time, there may be different types of clusters based on individual components or their chemical compounds.

Clusters are not conventional thermodynamic density fluctuations and are relatively stable formations with the structure close to FCC- and HCP- lattices whose lifetime τ_{cl}= (10-11)•10^{-9}s significantly exceeds the period of thermal oscillations of atoms. The local short-range order in the clusters is determined by nature and characteristics of interatomic interactions, as well as technological prehistory.

Unlike ordinary liquids, a stricter order covering several coordination spheres is naturally expected in systems with stronger interaction. In the cluster of this size the potential energy as a function of atomic positions, has a few lows. Thus allows to define this cluster in terms of a set of local states [12].

Such definition of local states is proposed in works [13,14], in which fluid is treated as a system consisting of local bulks, each of which can be in one of several configuration states. The potential polymorphism within this theory of liquids is considered in the work [15].

The smelt is approximated to the equilibrium state by a consistent positional disorder of clusters in the process of heating with the temperature over t_{an} (Figure 1). This approximation ends near the t_{cl}, i.e. the disordering temperature of the most thermally stable type of clusters and the equilibrium distribution of the elements within submicroscopic bulks of smelt [1].

In terms of the equilibrium distribution of atoms of different elements the proportion of newly formed clusters is increasing and they have energetically an advantage because of their smaller size and large crystallographic affinity between each other, which facilitates the emergence of centers of crystallization.

Cluster size reduction is accompanied by rise of intercluster volume or a disordered zone reaching to 15-45% of material volume. Compared with the clusters structural elements of the disordered zone consisting of several atoms have lower energy of the interparticle interaction, a medium-sized interatomic distance and less electronic density, contributing to alloys amorphization.

This features of the structure of liquid metals are due to changes of a structural factor and a radial distribution function of atoms at certain temperatures while preserving their general view that undoubtedly affects physical and chemical property values and their temperature dependences [1-4, 11,16].

In the process of frictional-resisted flotation the motion pulse is transferred from one atomic layer to another, without upsetting soundness and inter-particle bonds. Activation energy of the frictional-resisted flotation is the amount of energy of interatomic interaction, i.e. kinetic energy in motion.

The structure of metallic liquids is defined by two components, but they are not colloidal or emulsion systems and therefore clusters and the disordered area are involved in the frictional-resisted flotation. Strengthening of interatomic interaction in clusters increases the number of atoms in the frictional-resisted flotation and leads to input energy dissipation. In this regard, the dependence of ν (t) when cooling is characterized by elevated values of kinematic viscosity (Figure 1).

Surface tension (σ) of the alloy $Fe_{82}B_{12}Si_4C_2$ is determined by the concentration of surface active elements in the outer nuclear layer. The formation of the structure of the smelt in equilibrium distribution of atoms predetermines a more active participation of such elements in the process of cluster formation. The increase in the number of clusters leads to the decrease in the number of active elements in the surface layer, and as a result, the cooling polytherm is higher than the curve σ (t) during heating Figure 1), i.e. the surface tension increases.

The temperature-time treatment of smelt increases (Figure 1) specific electrical resistivity (ρ) and reduces magnetic susceptibility (χ). This is associated with increasing of interatomic bonds in clusters and the reduction of the number of charge carriers; with the reduction of cluster sizes and the increase in their number, i.e. the increase in scattering of conduction electrons; the increase in the density of

electrons in clusters and change of the valence of atoms in the outer layer of clusters and having high amplitude of thermal vibrations due to the weak interparticle interaction with other atoms in the cluster.

Thus, the temperature-time smelt treatment contributes to the formation of the equilibrium and microhomogeneous structure of the smelt. At this the liquid metal is more capable of supercooling and flows laminarly and dense when spinning. The lack of turbulence and splashing enables high-quality appearance of an amorphous film.

With ultra-fast hardening ($V \geq 10^6$ deg/sec) the main structural parameters of the initial smelt are maintained in supercooled liquids and in the amorphous film.

Compared to the serial production experienced technology enables to obtain a thicker amorphous ribbon where the outer surface is 3-5 times less (Figure 2) under the same spinning conditions. This positively affects not only the appearance of the material, but also improves its quality indicators. Such ribbons are characterized by a homogeneous and preferred structure in a cross section, and have more ductility in bending tests.

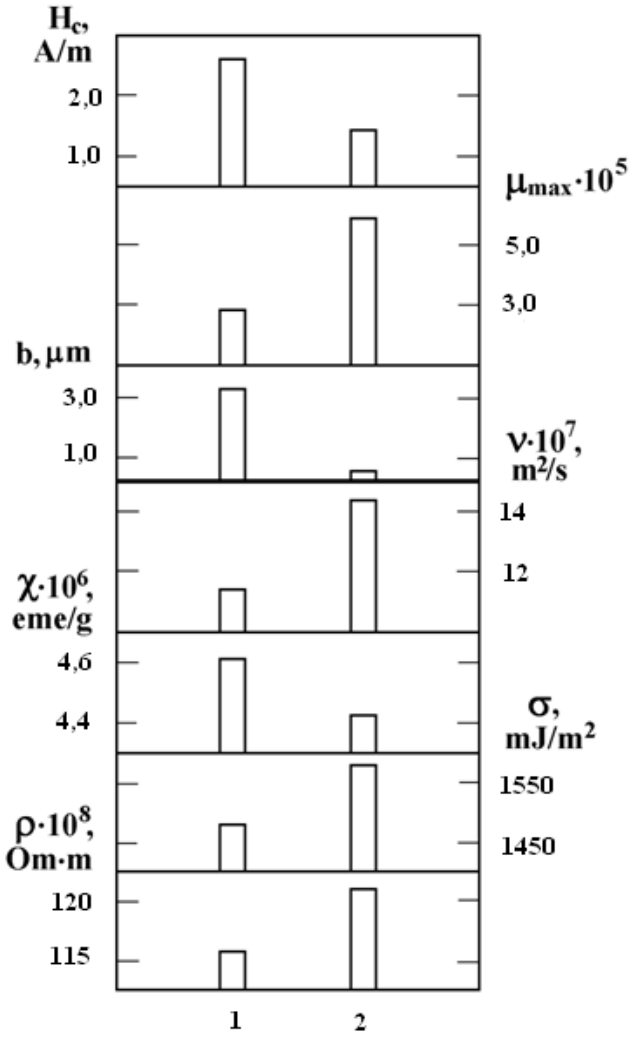

Figure 2. Effect of the smelting technology on the properties of $Fe_{82}B_{12}Si_4C_2$ alloy in the liquid (1300 °C) and amorphous states
1.- serial technology;
2.-pilot technology.

The last circumstance has important practical significance, as the amorphous ribbon is a starting material for the manufacture of various products. The workability of the ribbon increases with its plasticity, dissipation of deformation stresses in the material is improved, and high magnetic properties are maintained. [17].

The amorphous ribbons are used to obtain nano-and microcrystalline materials by annealing. To study the kinetics of the crystallization process a method of a differential thermal analysis (DTA) was used. In serial production and testing technology the crystallization process of the amorphous ribbons is characterized by a peak of heat deposition and is conducted in two stages (Figure 3).

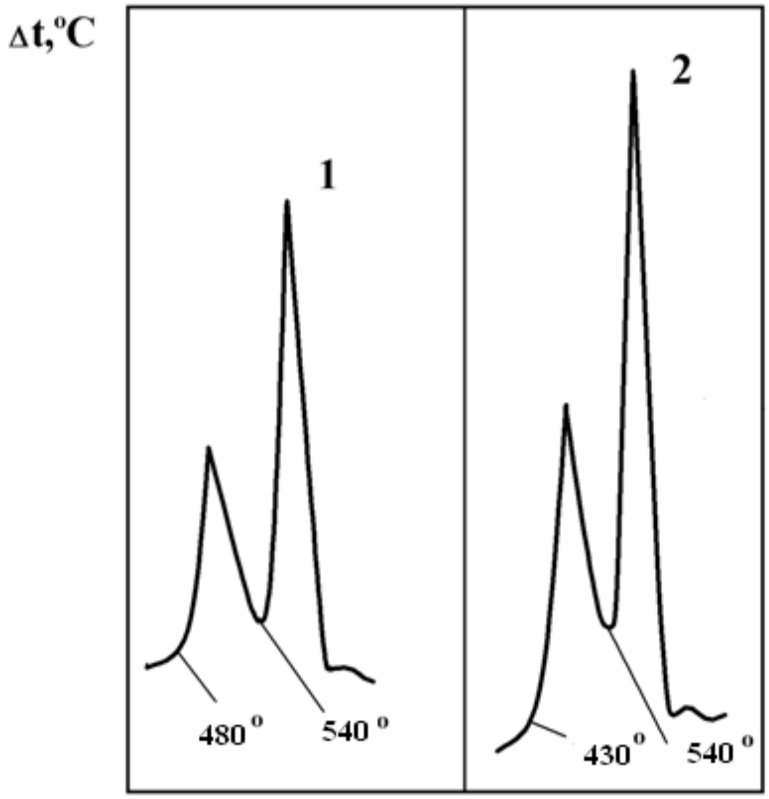

Figure 3. The results of differential thermal analysis of amorphous ribbon samples of $Fe_{82}B_{12}Si_4C_2$ alloy which have differences in the technology of smelting
1. - serial technology
2. - pilot technology

The temperature of the sample in the testing technology at which the first peak on the curve in the DTA appears is 50° higher than the temperature of the sample in a serial production, i.e. an amorphous ribbon structure which is obtained from the equilibrium smelt, has greater thermal resistance.

The comparative analysis of heat deposition peaks during crystallization process proves that the rate of amorphous state of ribbons is more stable when produced using TTP of the smelt. Such ribbons remain amorphous, with a thickness of 40 μm, and production-line ribbons when reaching a thickness of 30 μm and above become nano-and microcristalline, which negatively affects their plastic properties.

The data presented in Figure 2 shows that there is correlation dependence between structurally sensitive properties of the alloy $Fe_{82}B_{12}Si_4C_2$ in liquid state (ν, ρ, σ and χ) and quality characteristics of amorphous metal.

Summary Thus, the completed study shows that science-based technology of multi-component alloy smelting makes it possible to prepare equilibrium smelt, the structure of which has a significant effect on the properties of the amorphous ribbon before spinning and kinetics of its crystallization.
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