Nanotechnology for Obtaining Soft Magnetic Materials

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Abstract: Taking into account the concept of the quasi-chemical model of the liquid micro-non-uniform composition and the research made on the physical properties of the Fe-based melts being crystallized, the technology of the melt time-temperature treatment has been developed. Amorphous ribbons produced using this technology require optimal annealing temperatures to be specifically selected. The results of studying nanocrystalline magnetic core and their structure in the course of annealing at temperatures below and above the optimal ones are presented.

Keywords: Quasi-chemical model, time-temperature treatment, nanocrystalline magnetic core.

1. Introduction

The concept of the quasi-chemical model of the liquid micro-non-uniform composition is being developed under the supervision of B.A. Baum in our laboratory. According to it, the metal melt consists of space areas (groups, sibotaxes or clusters) within which the atom arrangement is characterized by certain ordering – short-range order. Due to moderately intense particles' heat movement, the clusters have no clear-cut boundaries: the atoms' ordered arrangement is being continuously replaced by another one, moving away from the cluster's core. For the same reason, the time of the given cluster's existence is limited and depends upon the chemical bonds' energy. At the same temperature, it is possible for two or more cluster ordering types to co-exist.

Any state of a macroscopic body is a result of the interaction of inter-particle forces and the heat motion of the structural elements making up this body. Specific features of the condensed state, making it contrasted to its gaseous one, imply that the heat motion is dominated by the inter-particle interaction, while, when it comes to the gaseous phase, the situation is opposite. Liquid as well as a solid body easily retains its integrity and its constant volume in the absence of external restrictions. In addition, both qualitatively and virtually quantitatively, inter-particle forces remain similar on either side of the melting interval. This is evinced by negligible qualitative changes in electron and phonon spectra of transition metal melts at Tmelt. [1], [2]. Besides, both in a metal liquid and a solid body, the essential structural elements are the same; these are atomic base structures and a quasi-gas of free electrons. As for the gaseous phase (metallic vapors), the structural elements are completely different, these are free electrons [3]-[5].

It is advisable to use the results achieved by B.A. Baum et al, these results were meant for cast crystal samples [6]. As a result of the research made on a large number of steels and alloys, the authors mentioned came to the conclusion that immediately after casting, liquid metals constituted essentially a non-homogeneous unbalanced system. Only overheating the melt up to reasonable "critical" temperatures (tk) specified by studying the polytherms of their physical properties results in a more balanced homogeneous state. To improve the quality of the metal cast it was proposed that the melt should be heated up to temperatures higher than the critical ones. An important addition to the existing technologies is the requirement of the isothermal melt held at T < Tliquid before pouring, which stabilizes some properties of the liquid metal and reduces the gases' concentration in the melt. The proposed production technologies resulted in significant improvement of mechanical, service and production characteristics of the hard metal. This method has been referred to as melt time-temperature treatment (TTT) casting. There is a good reason to believe that the melt subjected to time-temperature treatment and, as a result, turned out to become more homogeneous and balanced would easier become amorphous, with all other factors being equal, than any melt without TTT.

Taking into account the above concept and research made on the physical properties of the metal- and cobalt-based melts being crystallized, the unique technology of the melt time-temperature treatment has been developed. Amorphous ribbons produced, using this technology, require optimal annealing temperatures to be specifically selected [7], [8].

2. Experiment

The kinematic viscosity ν is one of the important characteristics of metal melts and the main values measured in case of torsional vibrations are recorded [9]. Determining these values by torsional vibrations is based on measuring the vibration factor δ. The number of models and programs is designed to calculate ν from the δ known. The calculation results of samples with different weights, geometry and density are compared with these calculations. The standard equipment to be used for measuring δ is not available. Thus, various engineering solutions have been used.

The amorphous ribbons were obtained by the planar flow casting process on a rotating disk (ribbons were 20-25 μm thick and 10 mm wide). Toroidal specimens of the 32 mm outer diameter and 20 mm inner diameter were wound out of these ribbons. The studies of $Fe_{72.5}Cu_1Nb_2Mo_{1.5}Si_{14}B_9$ specimens were carried out after annealing temperatures for 1 hour.

3. Results and Discussion

In the general form, the time-temperature treatment cycle is graphically represented in Fig. 1 in temperature-time coordinates. The most significant part is the establishment of the technological parameters, vis., the maximum temperature of heating Ttreat exposure time of the melt at this temperature (ttreat), the temperature of the metal before exiting from the furnace Texit. One variant of the procedure of determining ttreat is to measure the physical properties of the melt during its holding at Ttreat, which is somewhat higher than Tk. The relaxation time of the structure and stabilization of the properties can be recommended as the value of ttreat. Stirring the metal proves to be effective. It enables one to decrease the holding time at the critical temperature.

The typical temperature dependences of kinematic viscosity ν, electrical-resistance ρ, magnetic susceptibility χ, surface tension σ, and density d of the melt with a high amorphy causing elements' content are shown in Fig. 2. It is found that the special critical temperatures termed Tk are determined on basis of such data. Heating above Tk ensures a more homogenous melt state and, as a rule, causes the formation of the physical properties hysteresis. Overcooling of ΔT value is measured for this equilibrium melt. The presence of hysteresis is indicative for the differences between the initial and final melt states at Tk in the course of melting. Sometimes, the melt may be heated only up to the anomaly temperature Tan. The melt is held at the maximum heating temperature for a particular time during the experiment, investigating the time dependence of the properties changes at this temperature.

The kinematic viscosity (Fig. 3) of nanocrystalline magnetic alloy of Finemet type has been studied. The first regime of heating was up to the temperature below Tk, supplemented by quenching. The second regime was heating up to the temperature above Tk supplemented by quenching as in the first regime. The third regime is heating up to the temperature above Tk followed by overcooling and further quenching.

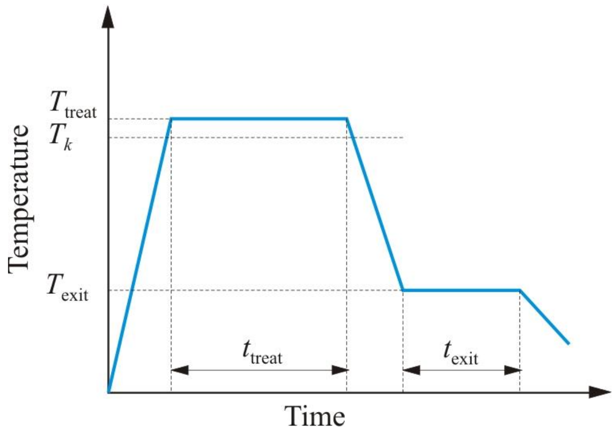

Fig. 1. Thermogram of the melting of a commercial metal depicting the temperature-time treatment of the melt.

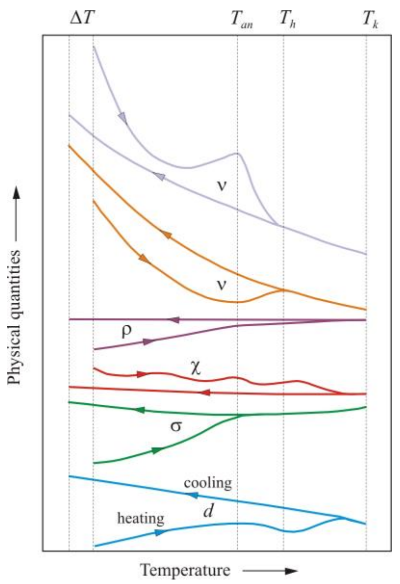

Fig. 2. The typical polytherms of physical properties of amorphous alloys: ΔT is a value of overcooling; Tan is the temperature of anomalies; Th is the temperature of hysteresis; Tk is the critical temperature.

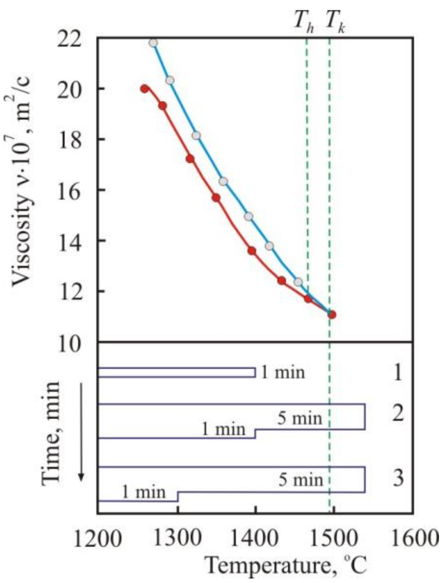

Fig. 3. The polytherm of kinematic viscosity of the amorphous Finemet type alloy: • is heating; o is cooling; Tk is critical temperature. The numbers near the curves denote the thermal diagrams of the three regimes.

The physical properties of nanocrystalline alloy versus the annealing temperature are shown in Table 1. The optimal properties are obtained by annealing at temperatures ranging from 542 to 572 °C. The maximum permeability and minimum coercive force are obtained during annealing at 542 °C for the nanocrystalline material.

In its initial state the alloy is x-ray-amorphous. The x-ray picture shows a blurred halo without additional crystal phases' reflections. When heated, melt crystallization occurs in one basic phase. One asymmetric exothermal peak is observed on the HTDT curve within the temperature range of 525-600 °C. After heat treatment at temperature 522 ^{o}C, against the background of the amorphous halo, peaks of the crystal component appear. The ordered solid solution Fe3Si, possessing the lattice parameter of a=0.56721 nm is the main crystalline phase. As the temperature increases, the amorphous phase halo intensity decreases, Fe3Si reflections intensity increases and superstructure reflections are most conspicuous. After heat treatment at temperature 542 ^{o}C, the alloy is essentially completely crystal; HTDT curves do not show any reactions with the evolution of heat.

Table 1. Magnetic Properties of Nanocrystalline Alloy as Function Annealing Temperatute

Annealing temperarures, T_a,^{o}C	$\mu_{0.08}$	μ_{max}	B_r/B_{800}	H_c, A/m
482	7300	147000	0.69	2.15
502	14400	330000	0.77	1.25
522	25000	394000	0.65	0.90
532	35000	540000	0.63	0.66
542	52000	713000	0.63	0.41
552	91000	663000	0.59	0.45
562	98000	664000	0.63	0.46
572	120000	688000	0.61	0.51
582	105000	588000	0.58	0.56
592	69000	430000	0.56	0.56
602	61000	237000	0.59	1.58

Fig. 4. shows histograms of the grains' sizes at different heating levels at temeratures 522 ^{o}C, 552 ^{o}C and 602 ^{o}C. The average grain size at these temperatures was equal to 7, 9 and 8 nm, respectively. With the temperature increase, however, the distribution of grain size changes. Low temperature of 522 ^{o}C is significant for the maximum grain size of 2 nm. These grains, with no clear boundaries, are, most likely, the nuclei (clusters) of the crystalline phase in the amorphous matrix. At the temperatures of 552 and 602 ^{o}C the grain size distribution is virtually identical [10]. At a higher temperature compared with the temperature of 522 ^{o}C, the proportion of grains is larger than 10 nm from 20.5% to 33.5%.

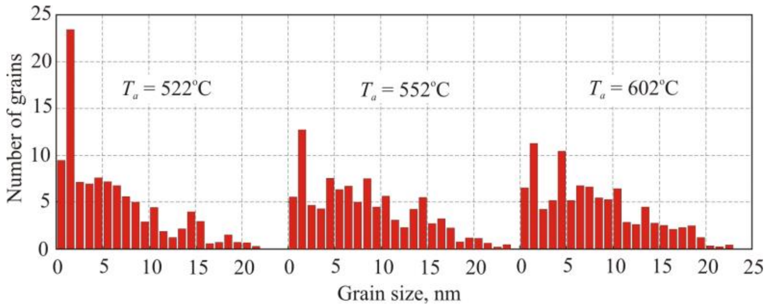

Fig. 4. Frequency distribution of grains by size detected after heat treatment at 522 ^{o}C, 552 ^{o}C and 602 ^{o}C for nanocrystalline alloy Fe72.5Cu1Nb2Mo1.5Si14B9.

In the nanocrystalline magnetic alloys Fe72.5Cu1Nb2Mo1.5Si14B9, low initial permeability corresponds to the structure, the share of which in the residual non-crystallized amorphous matrix is significant. The coercive force of the alloy at the annealing temperature of 522 °C is very low, i.e., in this area a low coercive force does not result in the high initial permeability. The highest initial permeability occurs when the structure is characterized by the largest volume of the ordered phase Fe3Si. Increasing the coercive force and decreasing the initial permeability at high temperatures are attributed to the formation of the magnetically hard phase Fe2B [11].

4. Conclusion

The implementation of the unity of the condensed substance state concept as applied to the description of the liquid structure is the notion of quasi-crystallizing. The modern implication of the notion deals with accepting the inter-particle interaction retaining the nature of forces (potentials) after melting: specific chemical features of various bonds, bonds' directionality elements, effects of multi-particle interaction, etc.

In studying the problems related to the actual Fe-based melts' properties and structure characterized by a complex relationship between valence electrons' localization and ability to collectivize and the properties and structure of the corresponding solid materials, the quasi-chemical model of the melt micro-non-uniform structure appears to be the most adequate. The model being beneficial is attributed to its retaining information on the actual connection between the liquid and solid states, and implies the possibility to forecast the results of physical-mechanical impacts on the melt, affecting the final product properties.

The state of multi-component commercial melts after completing the crystal-liquid phase transition is not, as a rule, equilibrium. There are temperatures of especially intensive structure changes for each melt. Heating melts up to these critical temperatures contributes to the system's change-over to the equilibrium state or the one close to it. The critical temperature values are set under laboratory conditions through studying the melt's properties temperature dependences. These values as well as the relaxation time do not depend upon the value of the volume studied as they are determined by the processes at the micro level occurring under kinetic conditions.

The proposed approaches which are scientifically justified enabled producing magnetic soft nanocrystalline magnetic core' possessing an extremely low coercive force (less than 0.5 A/м) and high initial magnetic permeability (more 100000) with the saturation magnetic induction of 1.2 T. The maximum relative magnetic permeability is more 600000.

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At present, the research team is undertaking the research projects from the National Natural science Fondation of China (NSFC), the Natural Science Fondation and Major Technology Innovation of Hubei Province.

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At present, the research team is undertaking the research projects from the National Natural science Fondation of China (NSFC), the Natural Science Fondation and Major Technology Innovation of Hubei Province.