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Kinetics of Thermal Relaxation of Cold Sintered Amorphous Powder of 82Ni18P

D. Minić[1,*], A. Maričić[2], N. Šušić[3]
[1] Faculty of Physical Chemistry, University of Belgrade, Belgrade, Yugoslavia
[2] Technical Faculty Čačak, Čačak, Yugoslavia
[3] Institute IMS, Belgrade, Yugoslavia

Abstract: *The process of thermal stabilization of cold sintered amorphous powder of 82Ni18P was studied using the method of measuring the electrical resistance in non-isothermal and isothermal conditions. It was shown that the process of crystallization followed by further structural arrangement occurs in stages in the temperature interval from 623 to 723 K. By measuring the change in electrical resistance at constant temperatures, T_1 = 613, T_2 = 633 and T_3 = 653 K, the kinetic parameters of the process of structural ordering of the evaluated substance were found. It was shown that every stage of crystallization is followed by a decrease in electrical resistance.*

Keywords: *Amorphous powder; Electrical properties; Thermal properties; Structural consolidation.*

Резюме: *Процесс термической стабилизации холодногоспеченного аморфного порошка 82Ni18P исследован методом измерения электрического сопротивления в неизотермических и изотермических усковиях. Показано, что процесс кристаллизации, сопровождаемый дальнейшим расположением структуры, происходит ступенчато в температурном интервале 623 – 723 K. Измерением электрического сопротивлениа при константных температурах T_1 = 613, T_2 = 633 и T_3 = 653 K определены кинетические параметры процесса стабилизации структуры исследованных образцов. Установлено, что каждый ступень стабилизации сопровождается соответственным понижением электрического сопротивления.*

Ключевые слова: *Аморфный порошок; электрические свойства; структурная консолидация.*

Садржај: *Методом мерења електричног отпора у неизотермским и изотермским условима испитан је процес термичке стабилизације хладносинтерованог аморфног праха 82Ni18P. Показано је да се процес кристализације, праћен даљим сређивањем структуре, одиграва ступњевито у температурном интервалу од 623 до 723 K. Мерењем промене електричног отпора на константним температурама T_1 = 613, T_2 = 633 и T_3 = 653 K одређени су кинетички параметри процеса стабилизације*

* Corresponding author: dminic@ffh.bg.ac.yu

структуре испитиваних узорака. Утврђено је да сваки ступањ кристализације прати одговарајуће смањење електричног отпора.

Кључне речи: *Аморфни прах; електрична својства; термичка својства; структурна консолидација.*

Introduction

Amorphous powders of metal alloys are a matter of constant interests to researchers [1-3], particularly from the point of view of their thermal stability and the crystallization process [4-8]. In our earlier work [5-8] the crystallization process of an amorphous powder of the NiP alloy was evaluated using DSC. In this paper, the crystallization process of an amorphous powder of the NiP alloy was evaluated by measuring the electrical resistance as a function of time at a constant temperature. The results are in accordance with earlier results [5, 8] obtained by DSC.

Experimental

For our research, we used a powder of the 82Ni18P amorphous alloy, which was obtained by electrolysis of the corresponding electrolyte water solution. The method of quantitative microstructural analysis was used to determine that the powder particle size is 0.66 - 1.73 μm, and that the greatest number of particles (~85 %) has a diameter between 0.85 and 1.4 μm. For the purpose of thermal characterization of the obtained powder, the analysis was done using differential scanning calorimetry (DSC).

For the purpose of evaluating electrical characteristics, the powder was pressed under 800 MPa into samples 4 mm in length and 0.5 mm^2 in diameter. Measurements of the electrical resistance as a function of temperature were performed using the four-point method in the temperature interval from 293 to 873 K. All experiments were done in argon atmosphere.

Results and discussion

The experimentally obtained dependence of electrical resistance on temperature ρ (T) of samples obtained by pressing the 82Ni18P amorphous powder is shown in Fig. 1.

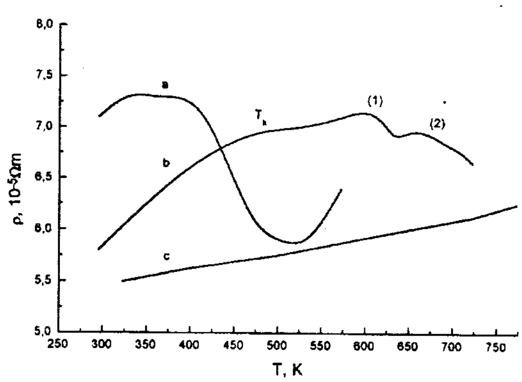

Fig. 1 Temperature dependence of electrical resistance of samples of the 82Ni18P pressed amorphous powder (a - first heating to 583 K; b - second heating to 873 K and c - third heating).

A DSC thermogram of the same sample is shown in Fig. 2. The DSC thermogram shows that this powder crystallizes in two steps, maximum 2 and 3, in the temperature interval from 620 to 720 K. Further exothermal structural ordering (maximum 3) follows the first crystallization maximum (maximum 2).

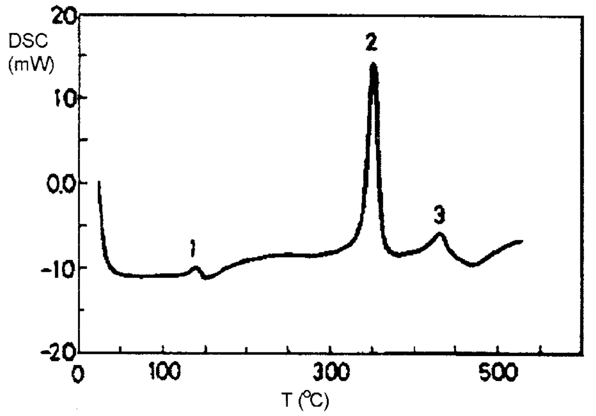

Fig. 2 DSC thermogram of the alloy in a hermetically closed capsule; the heating rate is 25 $Kmin^{-1}$.

By analyzing the curves shown in Fig. 1, it is concluded: during the first heating period, up to 583 K (a) a process of annihilation of defects, that were brought in during pressing occurs, which is then followed by a decrease in the specific electrical resistance of the sample after cooling, by 30 %.

The first heating of the sample was done only up to 583 K, to preserve its amorphous structure. During the second heating period (curve b in Fig. 1) a decrease in electrical resistance occurs in points (1) and (2), which are in the region of the crystallization temperature of the powder [5].

In accordance with [5], every crystallization step is followed by a decrease in the electrical resistance. By differentiating curve b it was found that dρ (t) / dt has a maximum at the temperature $T_k = 483$ K, which is the Curie temperature for this alloy. The decrease of the temperature coefficient of resistance at this temperature is a result of ending the interaction of conducting electrons with magnons.

The third heating of the same sample, (line c in Fig. 1) gives a linear temperature dependence of electrical resistance in the temperature interval from 273 to 873 K, which means that during the second heating period up to 873 K complete crystallization of the powder occurred.

The kinetic parameters of the crystallization process are determined using the method of measuring electrical resistance at a constant temperature. The acquired dependence of specific electrical resistance on time ρ (t) at temperatures 613 (curve a), 633 (curve b) and 653 K (curve c) are shown in Fig. 3.

A detailed analysis of the obtained experimental results showed that specific electrical resistance, at constant temperature changes in time according to equation:

$$\rho = \rho_0 e^{-k\tau}$$

where: ρ_0 – is the specific electrical resistance at the beginning τ, and k – is the rate constant. For example, in Fig. 4 a logarithmic dependence of lnρ on time τ, for the isotherm at 613 K, from Fig. 3, is shown.

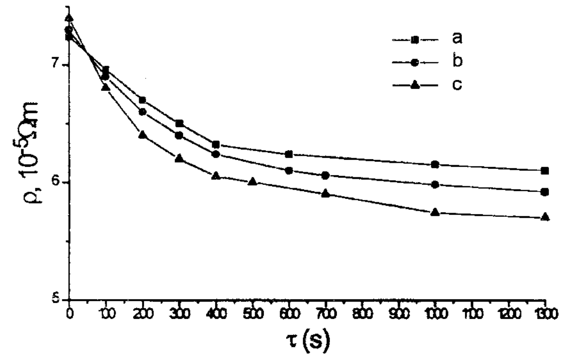

Fig. 3 Isothermal dependence of specific electrical resistance on time (curve a – 613, curve b – 633 and curve c – 653 K).

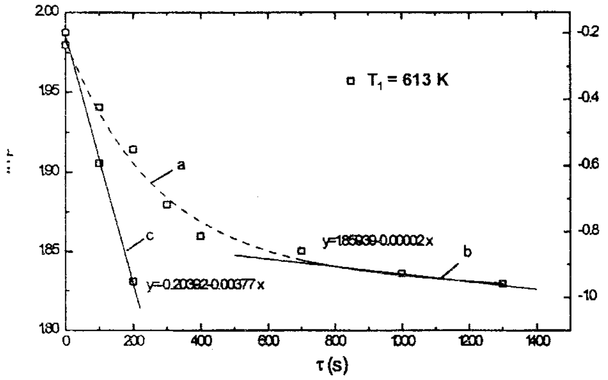

Fig. 4 Logarithmic dependence of specific electrical resistance on time at the temperature $T_1 = 613$ K.

From the shape of the curve in Fig. 4 it can be concluded that a complex process occurred during the isothermal decrease of electrical resistance. The curve is there after split into two components, b and c, whose time dependence is linear. The same procedure is used for dependence ρ (τ) at temperatures 633 K and 653 K, which is in the region of the crystallization temperature of the alloy.

From the slope $\Delta \ln \rho / \Delta \tau$, the rate constants for each crystallization step at given temperatures were determined. The energies of activation for both steps of crystallization were determined from the slope $\Delta \ln k / \Delta\,(1/T)$, Fig 5., using equation:

$$E = R\frac{\Delta \ln k}{\Delta(1/T)}$$

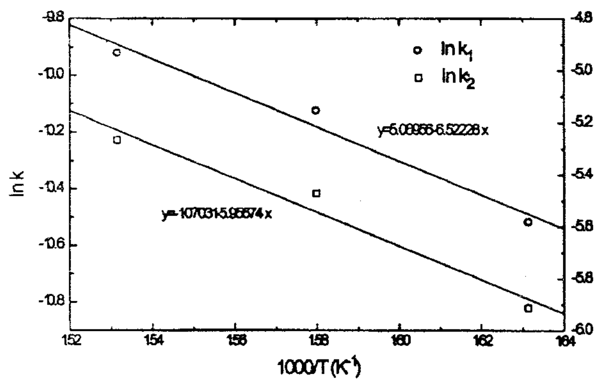

Fig. 5 Dependence ln k on (1/T) for every crystallization step.

The obtained values of kinetic parameters are shown in Tab. I.

Tab I. Kinetic parameters of the crystallization process of an amorphous powder of the 82Ni18P alloy.

T, K	$k_1 \cdot 10^{-3}$ s	$k_2 \cdot 10^{-5}$ s	E_1, kJ/mol	E_2, kJ/mol
613	3.77	2.00		
633	5.79	3.00	54.23	49.52
653	7.22	4.00		

Conclusion

Using the method of measuring the electrical resistance in non-isothermal and isothermal conditions in argon atmosphere it was determined that an amorphous powder of 82Ni18P crystallizes in steps in the temperature interval from 620 to 700 K. It was determined that every crystallization step is followed by a decrease in the electrical resistance, as a consequence of the increase in the mean free path of electrons.

By analyzing the dependence dρ/dT, the Curie temperature of the given alloy in its amorphous state was determined, $T_k = 483$ K, at which dρ/dT has a maximum as a result of ending the interaction of the conducting electrons with magnons.

It was experimentally determined that by pressing the powder at 800 MPa, the amorphous structure is retained.

During the process of sintering the stability of the amorphous structure is retained up to 560 K.

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