The crystallization kinetics of amorphous alloys[1]

S.D. Kaloshkin, I.A. Tomilin *

Moscow State Steel and Alloys Institute, Leninsky prosp., 4, Moscow, 117936, Russia

Abstract

The crystallization kinetics of Fe-based amorphous alloys was investigated by differential thermal analysis (DTA) and differential scanning calorimetry (DSC). Rather high values of activation energies were explained as a result of simultaneously correlated displacements of groups of atoms during the course of crystallization and allowed the correlation of amorphous alloys regarding their different composition. Connections between the temperatures, activation energies and thermodynamic driving forces were considered. Special attention was paid to the formation of nanocrystalline structures (Finemet).

Keywords: Crystallization kinetics; Activation energies; Finemet; Amorphous alloys

1. Introduction

The amorphous metallic alloys, a spacious class of materials, main attribute is an absence of the distant order in arrangement of atoms in their structure. In essence, the amorphous phase is an even more universal way of existence for a multi-component alloy, than crystalline structures. In the first approach it is possible to consider an amorphous alloy as two- or multi-components solid solution, like a liquid solution, but having the properties of solids. As shown by extensive experimental data, the amorphous state of an alloy is only due to the method of its production and preservation and it can be obtained practically in any multi-component system [1,2]. Under normal conditions the amorphous phases are unstable and at sufficient mobility of atoms pass to a crystalline state.

Amorphous alloys, as a rule, are obtained by the techniques of rapid quenching, mechanical alloying, vapour depositing and other methods, used for achieving strong

---

* Corresponding author.

[1] Dedicated to Professor Hiroshi Suga.

non-equilibrium conditions. Therefore for alloys obtained by different methods it seems to be natural for the relaxation processes of structure and properties at the annealing below the crystallization temperature. Similar relaxation processes are characteristic for crystalline materials, as well as for oxide glasses, received in conditions far from equilibrium.

Therefore, though the amorphous phases can change properties with time because of the relaxation processes, they can be considered as metastable, with definite properties for a given composition irrespective of a method of production.

The range of cooling rates of melts at which the formation of amorphous metallic phases can be observed is very wide. So, as for obtaining an amorphous state in a Fe-B system the necessary cooling rate is about 10^5–10^6 K/Sec [1], for the alloy $Zr_{65}Cu_{17.5}Ni_{10}A_{17.5}$ it is enough to only have 1.5 K/Sec [3]. The necessary cooling rate for obtaining amorphous alloys as well as thermal stability is determined both by thermodynamic driving forces of their transition into the crystalline state and mobility of atoms. The analysis of crystallization thermodynamics of amorphous alloys. Fe-B and Fe-Si-B systems is published in [4]. In this present work the main attention is paid to the analysis of kinetic parameters of the crystallization of amorphous alloys.

2. Theory

To estimate the ability of alloys to form amorphous phases and to define their thermal stability the kinetics of crystallization at heating is usually investigated. The most frequently used methods for this purpose is thermal analysis. Using various heating rates and continuously measuring one property, proportionally connected with degree of conversion, the dependence of conversion rate on temperature and time can be determined. Often the activation energy of transformation is determined from one of the kinetic equations reliable for the description of the crystallization process. For this purpose as equations usual for chemical reaction (1) [5,6], as the equations for solid-state conversions, in which are considered processes of nucleation and growth of particles of a new phase, are usually taken.

The equation for the description of constant rate nucleation processes and growth of three-dimensional particles (also with constant rate) [7] was for the first time offered by Kolmogorov. Then an equation of a more general kind, enabling the analysis of conversion kinetics for other laws of nucleation and growth (2) was proposed by Avrami[8]

$$d\xi/d\tau = k_0 \cdot \exp\left(-E_a/RT\right) \cdot f(\xi) \tag{1}$$

$$\xi(\tau) = 1 - \exp\left[-(k\tau)^n\right] \tag{2}$$

Where: $\xi(\tau)$ – degree of transformed volume, k_0 – frequency factor, E_a – activation energy, n – Avrami constant, $k = k_0 \cdot \exp\left(-E_a/RT\right)$.

In the most generalized kind of equation for kinetic analysis of solid state conversions proposed by Erofeev [9], no assumptions were made about the nucleation laws. There the probability (p) that a given infinitely small volume has passed conversion can

change depending on large variety of particular conditions of process

$$\xi(\tau) = 1 - \exp\left(-\int_0^\tau p\, d\tau \right) \tag{3}$$

Using various approaches for the transition to constant rates of heating v_i and the equations (1–3), by checking the characteristic temperatures T_i corresponded to the definite share of conversation ξ, we can obtain expressions for calculation of activation energy of process known as Ozava's equation (4) [10], Kissinger's (5) [11] and other, for example (6) [6].

$$ln\, v_i = -E_a/RT_i + C_1 \tag{4}$$

$$ln(T_i^2/v_i) = E_a/RT + C_2 \tag{5}$$

$$ln(T_i/v_i) = E_a/RT + C_3 \tag{6}$$

Here: C_1, C_2 C_3 – constants.

The linearity criterion of the experimental data plotting in the corresponding co-ordinates is usually taken as a proof of reliability of one or another equation. It was shown [12], that the activation energy, calculated from equations (4–6) are very close. Deviation makes not more than $2RT_{cr}$, that is, usually not more than 10% of E_a.

At the analysis of conversion kinetics of amorphous alloys by a non-isothermal method sometimes the equations, enabling to receive activation energy of process from the unique curve of thermal analysis, were used [13]. In this case, for example, the Borhardt's and Daniels's [14] and the Piloyan's [15] methods. A number of assumptions should be made to conclude that such methods could be used for given process. Application of them for processes taking place on grain boundaries and connected with nucleation and growth of particles of new phase should be done with great care, as they assume proportional dependence of the rate of conversion on a fraction of untransformed volume. Really for solid-state reactions the rate of conversion is proportional to the surface between old and new phases. These methods give comparable results with those received from equations (4–6) only in the cases of proportionality between the interphase surface and the fraction of untransformed volume.

Our analysis carried out for crystallization of amorphous alloys, for example for the alloy $Ni_{77}Nb_{10}B_{13}$, has shown that calculated activation energies by using methods given in [14, 15] are several times higher than the values obtained from equations (4–6).

The problem of the selection of a suitable equation for kinetic analysis of the crystallization process in amorphous alloys can be divided into two parts. The first is connected with the determination of geometrical probability of participation of atoms of an alloy in the crystallization reaction, revealing of the limiting stage of the process, the laws of nucleation and shape of growing particles [16–19]. The second is determined by the temperature dependence of the reaction rate, connected with probability of overcoming the activation barriers of elementary processes and the integration under nonisothermal conditions [16].

If the first problem is developed rather well, there are a number of books and survey works on this question (see for example [17–19]), then the second problem, in spite of

its apparent simplicity, has not developed so much. First of all it is due to the undefined nature of elementary processes and mechanisms of structure transformations which hinders treatment of data calculated using Arrenius's kinetic parameters. It however should be noted that the theoretical base for the decision of a given problem could be improved by an approach given by Eyring in the theory of rate process.

The activation energy of solid state transformations, proceeding through formation of nuclei and their growth, from the point of view of some researchers has not a physical sense but only empirical character [19]. It only establishes in practice the dependence of the rate of conversion on temperature. Nevertheless the comparison and analysis of activation energies obtained for various alloys should lean on treatment of their physical sense. It should pay self attention on high significances of activation energy of the process of amorphous alloys crystallization and consequently it should make three remarks in connection with its treatment.

Firstly there is the point of view that activation energy is some excess amount of energy belonging to one or a group of atoms in comparison with the average energy of atoms in a substance [18]. Therefore the opportunity for existence of the activation energy concept in solids is frequently subjected to doubt as far as it is very difficult, even in a very short time to imagine and the more so to prove, the concentration of excess energy in about several electron·volt in activated elementary complex of reaction. However there is no basis for such a point of view. Activation enrgy is not excess energy in relation to average value. It is the threshold value of energy above which the fluctuation of energy in the activation complex is sufficient for the elementary reaction to occur.

Secondly, the activation energy of the elementary act of crystallization of amorphous alloys does not belong to the one atom but more than likely to several atoms included in elementary complex of reaction. In solids there is very close contact between atoms, providing thermal balance in the smallest microvolume of an alloy. It would be incorrect to attribute all usually observable activation energy at the crystallization of amorphous alloys to one atom. Such energy would correspond to the temperature of atom in several thousand of degrees. With solid-state conversions, even in the case of jumps of single atoms, there is no necessity to attribute all the activation energy of the process to one atom making the jump. This energy can be spent, not for overcoming the activation barrier but, mainly for its downturn due to co-operative displacement of atoms [20]. And in experiments the total value of energy spent both to the downturning the potential activation barrier and to its overcoming is determined. The statement that the elementary act of solid state conversation is accompanied by simultaneous correlated displacement of groups of atoms [19, 20] is especially relevant to the process of crystallization of amorphous alloys, which is well described by the kinetics of viscous current possessing the simultaneous movement of atom collectives [21].

And thirdly, the crystallization of amorphous alloys is a very complicated process accompanied by nucleation and growth of various crystal phases under continuously varied conditions of chemical surroundings in a zone of conversion. Obviously, such a process occurs not only with the single value of activation energy and not by formation of a single configuration of activated complex. In practice with the multitude of probable ways of conversion only those mechanisms and activated complexes of the

crystallization process will be realized that are most probable at a given temperature, chemical and topological order in each microvolume of an alloy. Strong changes of crystallization conditions can result in a change of the mechanism and main activation complex of the crystallization process. So at an increase of heating rate of the amorphous alloy $Fe_{80}V_5B_{15}$ by more than 200 K/min. and, as a consequence there is a big increase of temperature, at which the crystallization occurs, the increase of activation energy from 275 kJ/mole up to ~ 500 kJ/mole is observed [22]. Thus, the high values of activation energy of crystallization of amorphous alloys first of all testify to plenty of atoms participating in the elementary act of structure reorganization. As the activation energy of process increases then the more atoms should simultaneously move in a definite direction at the elementary act of crystallization reaction.

3. Experimental results and discussion

The crystallization kinetics of amorphous alloys of systems Fe-B, Fe-M-B, Fe-Si-B and Fe-M-Si-B(where M-Al, Ti, V, Cr, Mn, Ni, Mo) depending on chemical composition were investigated by using DTA, DSC methods and electroresistivity measurement at continuous heating at not less than four constant heating rates (4, 8, 16, 32 K/min.). The alloys were produced by spinning method of quenching the melt on a rotated drum with cooling rate of 10^5-10^6 K/s as ribbons of 20–25 μm thickness.

Crystallization of investigated alloys usually passes in two stages, on the first of which the formation of crystalline solid solution based on α-Fe (ferrite) in an amorphous matrix takes place. On the second, there is the decomposition of the remaining amorphous matrix with simultaneous formation of ferrite, boride and silicide phases. For some alloys the stage of formation of primary crystals of ferrite was not observed and crystallization passed in one stage corresponding to the second stage of conversion. Fig. 1 show the typical DSC curves for crystallization of amorphous alloys for each of these cases. In Table 1 are the results of calculations for the activation energies for each of the crystallization stages E_1 and E_2, made using the equation (5), are shown as well as the temperatures T_1 and T_2 corresponding to appropriate maximum rates of conversions for each of the stages. The error of calculation of activation energies was determined as a root-mean-square deviation multiplied on Student's coefficient for the probability 0.95. There, where the error is not specified, it can be accepted equal to $\sim +/-10\%$.

The data in Table 1 for specified alloys is in general similar to that published in scientific literature. The complete coincidence should not be expected because of the dependence of activation energy on technological parameters in the production of alloys (cooling rate, quality of ribbon's surface, atmosphere of quenching, impurities and other). So, for example, the kinetics of crystallization of ribbons of different thickness (14, 24 and 35 μm) of the amorphous alloy $Fe_{70}Cr_{15}B_{15}$ was investigated. The crystallization onset temperatures of these alloys slightly decreased at an increase of thickness, the heat of crystallization was the same at ~ 7.2 kJ/mole. However the activation energies differed -400, 310 and 280 kJ/mole, specifying appreciable influences of quenching rates to activation energy. Thus the quantitative analysis of kinetic
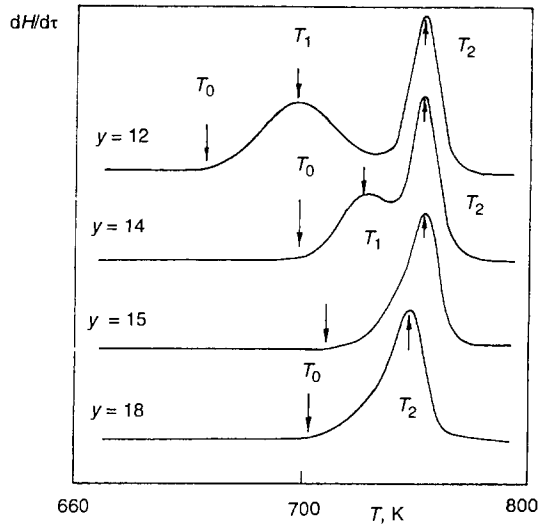
Fig. 1. DSC curves of dependences of the heat flow $-dH/dt$ on temperature for crystallization of amorphous alloys $Fe_{90-y}Cr_{10}B_y$ scanned at the heating rate 8 K/min. T_0, T_1 and T_2 are the temperatures of onset, the first and second apexes of DSC heats, respectively,

parameters of crystallization of amorphous alloys is possible only with careful reproduction of the technological parameters for their production. Nevertheless the comparison of the kinetic data for large groups of amorphous alloys of different compositions obtained under close technological conditions is quite possible.

The consideration of data given in Table 1 reveals the main regularities of dependencies of activation energy on the chemical composition.

1. Activation energy for the stage of solid solution formation E_1 was as a rule less than for the stage of eutectic decomposition E_2. It means that the mechanism of formation of a crystalline phase on the basis of metal component requires simultaneous movement of a smaller quantity of atoms in the elementary act of crystallization reaction than at the formation of the complex phases of a boride type. At the same time the second stage of crystallization is characterized by a larger thermodynamic stimulus than the first ($\Delta G_1 < \Delta G_2$–Fig.2) [23]. The passage of the crystallization from a two stage to a one stage process at the increase of metalloid concentration is observed at the certain relations of driving thermodynamic forces $\Delta G_1/\Delta G_2$ and activation energies E_1/E_2 of crystallization process. So for alloys $Fe_{100-y}B_y$ and $Fe_{90-y}Cr_{10}B_y$ the specified relations are 0.6 and 0.8 at boron concentration 17 and 15 at.% respectively. Just at these concentrations the maximum values of activation energy and crystallization temperature occur.

2. For the stage of initial formation of a solid solution it is possible to consider, as the limiting factor of crystallization, the mobility of atoms in the amorphous matrix. If to accept, that crystallization of an alloy begins at achievement of viscosity of an amorphous phase of some definite value it is possible to establish a proportional

Table 1.
The stages temperatures (K) and the corresponded activation energies (kJ/mole) of crystallization of iron-based amorphous alloys

n/n	Alloy	T_1	T_2	E_1	E_2
1.	$Fe_{88}B_{12}$	650	758	128	245 ± 8
2.	$Fe_{87}B_{13}$	642	753	164 ± 14	245 ± 8
3.	$Fe_{85}B_{15}$	687	741	186 ± 6	294 ± 20
4.	$Fe_{83}B_{17}$	–	722	–	288 ± 11
5.	$Fe_{80}B_{20}$	–	708	–	206 ± 8
6.	$Fe_{83}Cr_2B_{15}$	698	744	203 ± 8	350 ± 20
7.	$Fe_{80}Cr_5B_{15}$	718	747	232 ± 6	360 ± 20
8.	$Fe_{77}Cr_8B_{15}$	–	747	–	355 ± 20
9.	$Fe_{75}Cr_{10}B_{15}$	–	756	–	350 ± 25
10	$Fe_{73}Cr_{12}B_{15}$	–	756	–	336 ± 20
11.	$Fe_{70}Cr_{15}B_{15}$	–	764	–	310 ± 25
12.	$Fe_{67}Cr_{18}B_{15}$	–	779	–	278 ± 15
13.	$Fe_{78}Cr_{10}B_{12}$	700	756	208 ± 7	326 ± 10
14.	$Fe_{76}Cr_{10}B_{14}$	730	756	260 ± 25	395 ± 25
15.	$Fe_{72}Cr_{10}B_{18}$	–	750	–	288 ± 30
16.	$Fe_{80}Al_3B_{17}$	732	759	254 ± 8	365 ± 35
17.	$Fe_{80}V_3B_{17}$	735	762	265 ± 12	445 ± 30
18.	$Fe_{80}Ti_5B_{15}$	735	850	243 ± 20	?
19.	$Fe_{80}V_5B_{15}$	731	800	275 ± 10	?
20.	$Fe_{80}Mn_5B_{15}$	712	768	226 ± 12	500 ± 25
21.	$Fe_{80}Ni_5B_{15}$	687	750	188 ± 12	305 ± 15
22.	$Fe_{75}Cr_5B_{20}$	–	726	–	232 ± 20
23.	$Fe_{75}Mn_5B_{20}$	–	752	–	290 ± 10
24.	$Fe_{72}V_{10}B_{18}$	–	806	–	345 ± 40
25.	$Fe_{80}Si_5B_{15}$	780	797	405 ± 30	475 ± 35
26.	$Fe_{78}Si_9B_{13}$	799	833	285	260
27.	$Fe_{77}V_3Si_5B_{15}$	780	803	370 ± 15	520 ± 30
28.	$Fe_{77}Cr_3Si_5B_{15}$	795	818	460 ± 25	495 ± 20
29.	$Fe_{77}Mn_3Si_5B_{15}$	776	801	440 ± 30	445 ± 25
30.	$Fe_{77}Co_3Si_5B_{15}$	775	800	355 ± 25	425 ± 35
31.	$Fe_{75}Ni_3Si_9B_{13}$	791	887	203	200 ± 10
32.	$Fe_{75}Mo_3Si_9B_{13}$	833	893	325 ± 30	390 ± 15
33.	$Fe_{75}Cr_5Si_5B_{15}$	803	873	300 ± 20	225
34.	$Fe_{70}Cr_{10}Si_5B_{15}$	811	901	260 ± 25	220
35.	$Fe_{77.5}Si_{13.5}B_9$	820	834	390 ± 30	390
36.	$Fe_{77}Si_{13.5}Cu_{0.5}B_9$	755	826	320 ± 20	410
37.	$Fe_{76.5}Si_{13.5}Cu_1B_9$	746	826	280 ± 20	390
38.	$Fe_{75.5}Si_{13.5}Cu_1Nb_1B_9$	764	854	300 ± 30	?
39.	$Fe_{73.5}Si_{13.5}Cu_1Nb_3B_9$	825	990	360 ± 30	690

relation between the temperature and the activation energy of formation of α-Fe primary crystals in amorphous matrix [21,24]. The proportional relation between E_1 and T_1 was found, for a large group of alloys, to have a similar chemical basis (Fig. 3). For the second crystallization stage such a phenomenon was not found, though there was the tendency of an increase of crystallization temperature with an increase of activation energy.
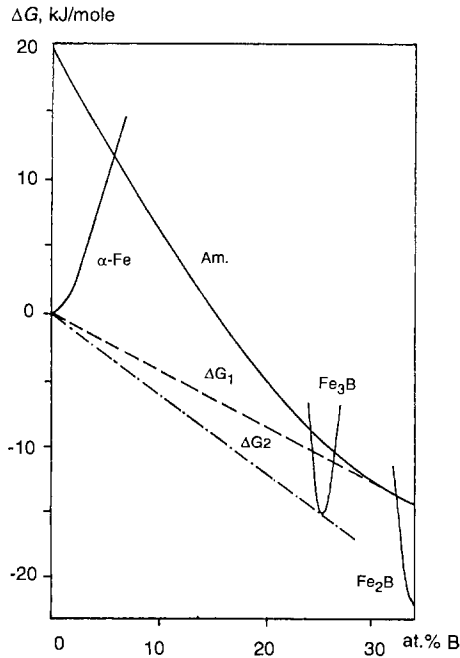
Fig. 2. The thermodynamic moving forces for crystallization of Fe-B amorphous alloys for primary α-Fe precipitation (ΔG_1) and eutectic decomposition (ΔG_2)

3. Complication of the chemical composition, as a rule, results in the increase of activation energy of crystallization. Silicon and transition metal additions to Fe-B alloys results in a strong increase of activation energy of the first as well as the second stages. It is called by that alloying elements should be redistributed between forming phases at the crystallization and for this purpose more quantity of atoms should be involved into the elementary act of reorganizing the structure. So, for example, Mössbauer speectroscopy investigations of the alloy $Fe_{78}Si_9B_{13}$ has shown that after the first stage of crystallization the ferrite phase contained more silicon in the structure (~ 14 at.%) than in the initial amorphous alloy [25]. The research on amorphous alloys of the Fe–Cr–B system have shown that, in this alloy, after the first stage of crystallization the ferrite phase contains less chromium than the initial amorphous phase [26].

At the kinetic analysis of conversions, from the position of the theory of rate process, the constant of balance of transitive complexes with the initial substance as well as with the products of reaction is calculated [18]. Such an approach, besides the dependence of reaction rate on activation energy of conversion, in particular means the dependence of conversion rates on the different formation enthalpies of initial and final products of the reaction. With reference to the process of amorphous alloy crystallization it specifies a possible connection between temperature and heat of crystallization. The
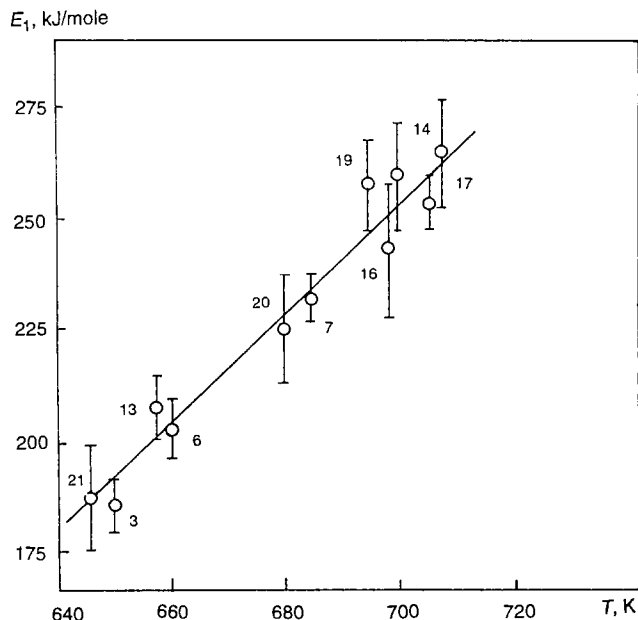
Fig. 3. The connection between the initial temperatures of crystallization and the activation energies corresponding to this temperatures for amorphous alloys $Fe_{100-x-y}M_xB_y$, which crystallize in two stages. The numbers of points correspond to those listed in Table 1.

analysis of crystallization of amorphous alloys of close composition based on iron has revealed such a connection [23]. And as for alloys of different composition it has a correlation character (Fig. 4) for alloys with the identical basis, for example $Fe_{75}M_5B_{20}$ their functional dependence can be found (Fig. 5).

Pays on self attention the similar behaviour of dependencies of the heat and the activation energy of crystallization of amorphous alloys of the same composition basis. On Fig. 6 the data of the influence of alloying elements on the heat (a) and the activation energy of crystallization (b) are indicated. Comparison of the curves specifies the connection between the kinetic and the thermodynamic factors of crystallization: as the potential hole of atoms positioned in the structure becomes deeper, the higher the barriers for transition of atoms to other positions become. The similar connection between the heat of crystallization and the activation energy values for Co-Fe-Si-B amorphous alloys was noted too [27].

4. The characteristics of crystallization kinetics of the Finemet type amorphous alloys

The addition of active surface elements can essentially influence the crystallization kinetics of amorphous alloys. There is an interesting, and important for practice,
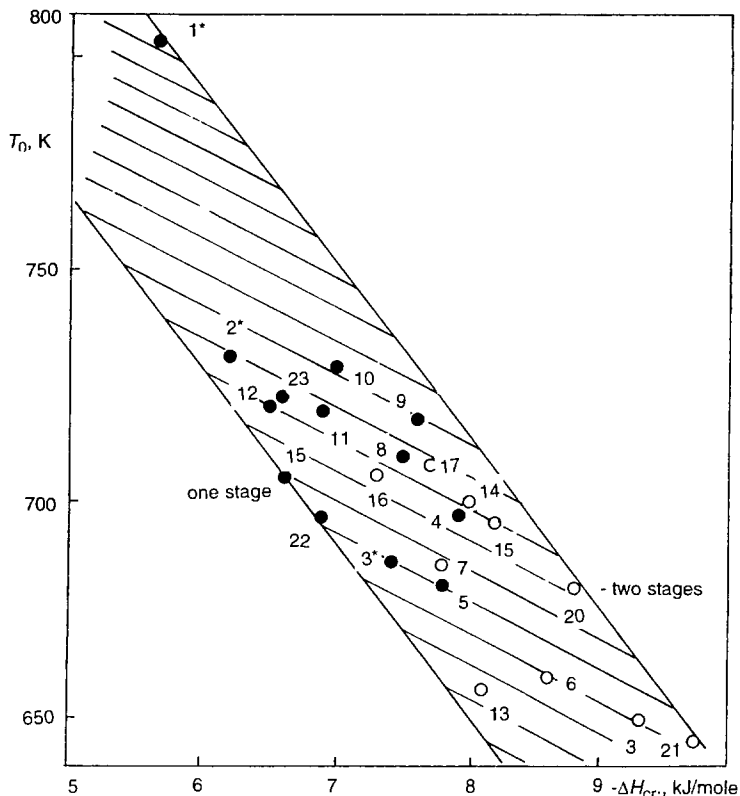
Fig. 4. The correlation between the heats and the temperatures of crystallization for amorphous alloys Fe-M-B (heating rate 8 K/min). The number designation corresponds to Table 1, 1* -Fe$_{75}$Ti$_5$B$_{20}$, 2* –Fe$_{75}$V$_5$B$_{20}$, 3*–Fe$_{75}$Ni$_5$B$_{20}$.

example of the influence of alloying elements on the crystallization kinetics of the "Finement"type of alloys with nanocrystalline structure obtained by the crystallization of the amorphous phases of Fe-Si-Cu-Nb-B system (Fig. 7) known as soft magnetic materials. This alloy crystallizes in two stages: first - the formation of the α-Fe enriched by silicon with crystals the size of 10-20 nm; second the boride phase takes place. If the alloy Fe$_{77.5}$Si$_{13.5}$B$_9$ crystallizes with activation energy of the first stage, 390 kJ/mole, additions of 0.5 and 1 at.% of copper lower this value up to 320 and 280 kJ/mole respectively . At the same time the crystallization temperature is lowered too [28]. The activation anergy of the second stage of crystallization remains practically the same and is about 400 kJ/mole.

The further addition of 3 at.% Nb increases the activation energy of crystallization almost up to it's value for the amorphous alloy without Nb and Cu additions –360 kJ/mole. Niobium having stabilized the amorphous phase strongly hinders redistribution of boron between the amorphous phase and α-Fe at crystallization and reduces the
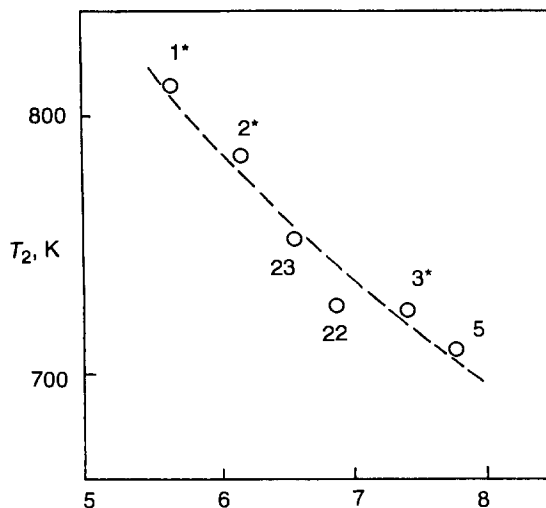
Fig. 5. The connection between the temperatures of peaks and the heats of crystallization of $Fe_{75}M_5B_{20}$ (heating rate 8 K/min). Point designation follows Fig. 4 and Table 1.

rate of growth of α-Fe particles. But the Nb additions have an especially strongly effect on the second stage of crystallization. The activation energy of this stage grows up to 690 kJ/mole by strong increase of the stage temperature. So high activation energy specifies a very strong correlation with displacement of atoms at the second stage of crystallization and that the elementary act of structure reorganization requires simultaneous displacement of a sufficient number of atoms.

The crystallization heat of the amorphous alloy $Fe_{77.5}Si_{13.5}B_9$ with the additives of 1% of copper and 3% of niobium was found to be two times lower than for the alloy without additions and makes about 2 kJ/mole. Such strong influence of additions on the crystallization heat can reflect the influence of chemical composition on the enthalpies of formed phases as well as an increase of formed phases enthalpies due to the great value of interphase surfaces in nanostructures. If to admit that all reduction of crystallization heat is only connected, with the contribution of the surface energy, into the enthalpy of forming an amorphous matrix α-Fe particles with the size 15 nm, the calculated value of surface energy will be about 0.90 J/m^2. The estimated value of interface energy for α-Fe at 800 K is about 1.15 J/m^2 [29]. It is known that the copper additives strongly decrease the surface energy of α-Fe crystals becoming stronger as the temperature lowers [28]. The extrapolation of data [29] to 800 K gives for α-Fe, with 0.1% Cu the value of surface energy, about 0.70 J/m^2. Thus there is a correlation between the value of surface energy in α-Fe alloyed by copper and the value estimated from the data of crystallization heat reduction. The surface energy reduction seems to be the main reason for the facilitation of precipitation of α-Fe particles and the corresponding downturn in temperature and activation energy of crystallization process.
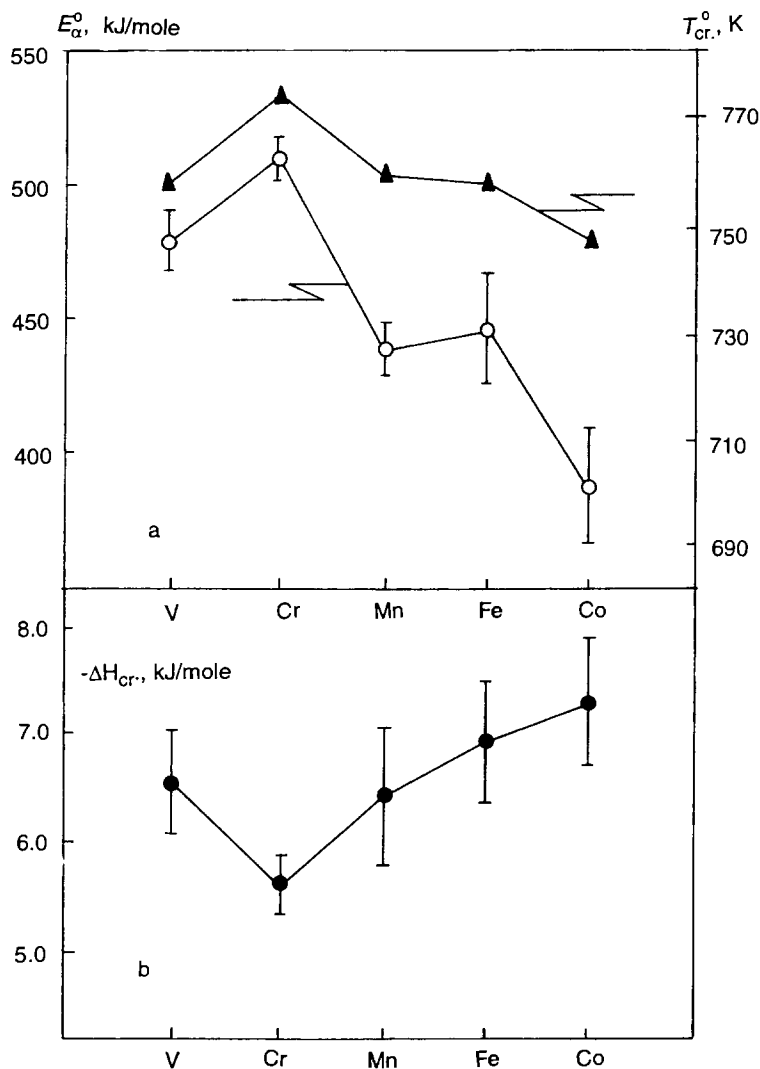
Fig. 6. The dependencies of the heat of crystallization (a) and the corresponding activation energies and temperatures (b) on the arrangement of additional elements in the Mendeleev's table for amorphous alloys $Fe_{77}Si_5M_3B_{15}$ (heating rate 8 K/min).

As far as the expression for the nucleation rate is an exponential function of surface energy and this one appear in the index as the third power [17] the reduction of this value should result in essential reduction of activation energy of this process. The simple estimation shows that the thermodynamic motive force for pure iron particles with size ~15 nm formation, because of the contribution of surface energy, is
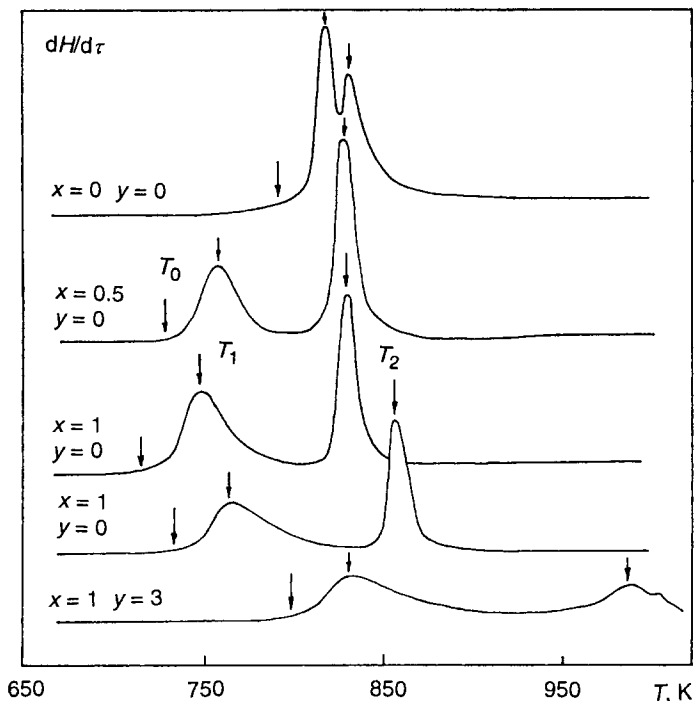
Fig. 7. DSC curves of crystallization for "Finemet" -type amorphous alloys $Fe_{77.5-x-y}Si_{13.5}Cu_xNb_yB_9$ at the heating rate of 16 K/min; designation as in Fig. 1.

essentially less in comparison with the case of the formation of large particles. However in the case of copper additions to the alloy this reduction is not so essential. It explains the transition from the eutectic crystallization of alloys of the Fe-Si-B system to primary precipitation of α-Fe for alloys containing copper. Estimation shows that the copper additions also essentially reduce the critical size of nucleating centres which for alloys both with and without copper has values of 8 and 5 nm accordingly. The work of forming a nucleating centre of critical size is reduced by about 3 times through copper additions to the amorphous alloy.

In particular one of the possible reasons for the stabilization of amorphous-crystalline structure could be the significant pressure on the grain boundaries at crystallization of the amorphous phase which relaxation is delays from its increase. This pressure can increase the surface energy of formed particles and blocks their further growth [30]. The increased amount of a crystalline phase at the "Finemet" type amorphous alloys annealing occurs mainly due to the formation of new particles quickly growing up to almost the final sizes. As a result after the first crystallization stage the nanocrystalline amorphous-crystalline structure that is stable in a wide temperature interval is formed.

15. Conclusion

The analysis of the stability of amorphous alloys should take into account both the thermodynamic and the kinetic factors of crystallization. These factors are connected. In the first stage of precipitation the crystals of a solid solution in amorphous matrix are connected with correlated displacement of smaller number of atoms, than the corresponding stage in eutectic crystallization. Complication of chemical composition, blocking the surface of growing particles by atoms, not participating in formation of new phases and other factors causing the necessity of correlated moving of different atoms, result in the increased activation energy of the crystallization process.

Acknowledgements

References

[1] H.A. Davies, Proc. 3d Int. Conf., Rapidly Quenched Metals, Brighton, 1978, p. 3.
[2] H. Jones, Proc. 8th Int. Conf., Rapidly Quenched and Metastable Materials, Sendai, 1993, p. 1.
[3] T. Masumoto, Proc. 8th Int. Conf., Rapidly Quenched and Metastable Materials, Sendai, 1993, p. 8.
[4] S.D. Kaloshkin, I.A. Tomilin, J. of Phys. Chem., Russia, 70, (1996) p. 27. (in Russian).
[5] C. Antonione et al., Z. Metallk., 75 (1984) 714.
[6] J. Sestak, Thermochim. Acta, 98 (1986) 339.
[7] A.N. Kolmogorov, Izvestiya Akademii Nauk, USSR. Ser. Matematika, 1937, N3, p. 355 (in Russian).
[8] M. Avrami, J. Chem. Phys., 7 (1939) 1103.
[9] B.V. Erofeev, Doklady Akademii Nauk, USSR, 1946, v.52, p. 515 (in Russian).
[10] T. Ozava, J. of Therm. Anal., 2 (1970) 301.
[11] H.E. Kissinger, Anal. Chem., 29 (1957) 1702.
[12] S.D. Kaloshkin, I.A. Tomilin, A.K. Zaytsev, in Struktura, structurnye prevrasheniya i magnitnye svoystva amorfnyh metallicheskih splavov, M: Metallurgiya, USSR, 1986, p. 67 (in Russian).
[13] N.Sh. Petro, B.S. Girgis, Thermochimica Acta, 127 (1986) 127.
[14] H.J. Borchadt, F. Daniels, J. Phys. Chem., 79 (1957) 41.
[15] G.O. Piloyan and O.S.Novikova, J. of Inorganic Chem., 12, (1967) p. 313 (in Russian).
[16] T. Kemeny and J. Sestak, Thermochim. Acta 110 (1987) 113.
[17] J.W. Christian, Transformations in Metals and Alloys, Pergamon Press, Oxford, 1965, v.1.
[18] M.E. Brown, D. Dollimore and A.K. Galwey. Reactions in The Solid State, in the ser.: "Comprehensive Chemical Kinetics", 1980, v.22.
[19] J.Sestak, Glasses; Phenomenology of vitrification and crystallizaation, in Z. Chroj, J. Sestak and A. Triska (Eds.), Kinetic Phase Diagrams, Elsevier, Amsterdam 1991, p. 169.
[20] J. Sestak, Thermochim. Acta 110 (1987) 427.
[21] S.D. Kaloshkin, I.A. Tomilin and F.D. Hoang, Fis. Met. Met., USSR, 1987, v.63, p. 202 (in Russian).
[22] A.A. Zubkov, S.D. Kaloshkin, I.A. Tomilin, Izvestiya vuzov. Chernaya Metallurgiya, USSR, 1989, N7, p. 69 (in Russian).
[23] I.A. Tomilin and S.D. Kaloshkin., Fis. Met. Met., USSR, 1989, v.68, p. 518 (in Russian).
[24] K.H.J. Bushow, J. Phys. F: Met, Phys., 13 (1983) 563.

[25] S.D. Kaloshkin, V.P. Ovcharov, I.A. Tomilin, F.D. Hoang, Proc. 6th Non-Ferrous Metallurg. Symp. Sec. B Rap. Sol. Mat., Oct. 11–13, 1989, Hungary, p. 92 (in Russian).

[26] S.D. Kaloshkin, L.A. Alekseev, I.A. Tomilin, F.D. Hoang, Docl.Acad. of Sci. USSR, 1985, v. 284, p. 1120 (in Russian).

[27] O.Ya. Vasiljeva, I.A. Tomilin and I.B. Kutsenok, Nanostructured and Non-Crystalline Materials, 1995, World Sci. Publ., p. 362.

[28] S.D. Kaloshkin, I.A. Tomilin, B.V. Jalnin, I.B. Kekalo, E.V. Shelekhov, Sci. Forum, 179/181 (1995) 557.

[29] V.A. Lazarev, The Influence of Surface Active Elements on the Diffusion of Copper and Iron in the Bulk and Grain Boundary of Iron, Thesis, Moscow, 1973 (in Russian).

[30] T.Yu. Mochalova, S.D. Kaloshkin, I.A. Tomilin, E.V. Obrucheva, B.V. Jalnin, Proc. Int. Symp., Mechanically Alloyed and Nanocrystalline Materials, Quebec, 1995, (Unpublished).