THE ZINC PENETRATION ALONG TILT GRAIN BOUNDARY 38° [100] IN Fe-12at.%Si ALLOY NEAR ORDERING A_2 - B_2 IN THE BULK

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Introduction

In their previous work, the authors studied the process of penetration of tin and zinc along tilt grain boundaries 43° [100] in the bicrystals of bcc alloy Fe-5at.%Si [1]. In the whole studied temperature range, wetting and the region of rapid diffusion are observed simultaneously on grain boundaries in the alloy Fe-5at.%Si. When the samples are subjected to high pressure, the wetting disappears at about 0.5 GPa [2]. The region of accelerated diffusion between the bulk solubility limit of zinc C_o and a concentration C_{bt} disappears simultaneously. The experimental data obtained by us in [2], along with the results of [1],provide evidence that at C_{bt} a premelting transition occurs on the grain boundary which leads to the formation of a thin thermo-dynamic equilibrium interlayer of quasi-liquid phase on the grain boundary. There exist a number of theoretical works where such phase transitions on interfaces accompanying wetting are predicted [3-5].

All necessary conditions for a premelting transition to exist are satisfied in the studied system: high positive value of enthalpy of mixing of solution components, wetting of grain boundaries in the two-phase region, "solid-melt" as well as the fact that the phenomena mentioned are observed on grain boundaries of the component having higher temperature of melting (iron). Therefore, it is quite reasonable to say that we do observe a premelting transition on grain boundaries.

The aim of the present paper is to determine how the phase transition of concentration ordering in the bulk affects the process of zinc penetration along the grain boundaries in the system Fe-Si, the grain boundary wetting and premelting transition.

Experimental

To perform the experiments, a bicrystal of alloy Fe-12at.%Si with tilt grain boundary 38° [100] was grown. In this alloy atomic ordering of the solid solution iron-silicon occurs: when the temperature is decreased, the disordered bcc lattice (A_2 structure) is transformed into the ordered one (B_2 structure) [6].It was cut on a spark cutter into samples of length 6...12 mm and cross-section 1.5 x1.5 mm. The grain boundary was disposed in the middle of the sample,perpendicularly to its longer part. The zinc layer was applied to the sample by immersion into melt. The prepared samples were soldered in evacuated silica ampules,then annealed in an oven in temperature 714....994°C.

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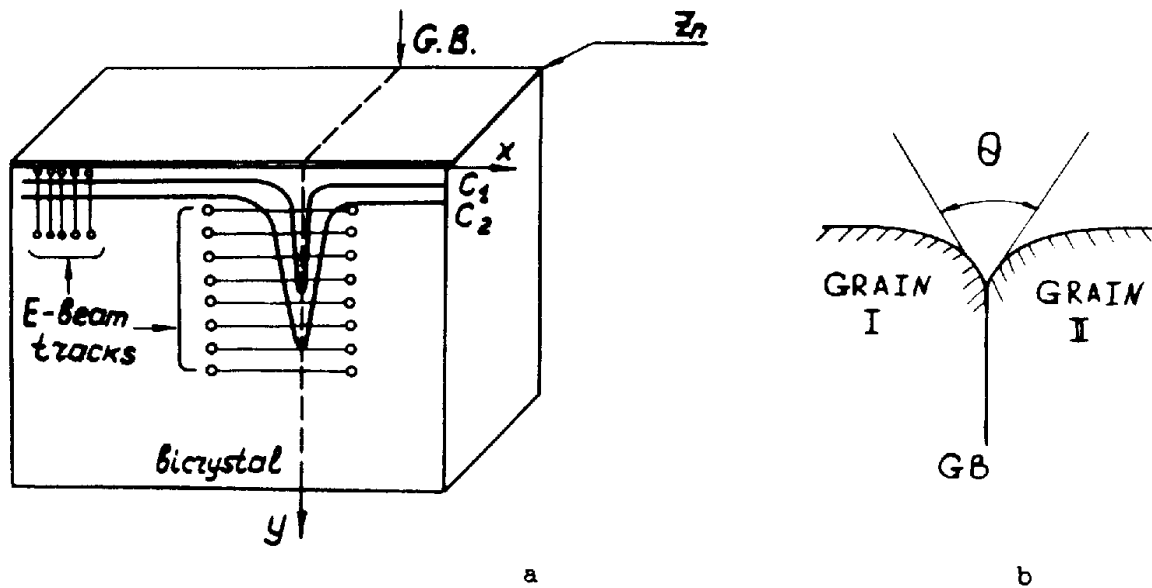a   b

Fig.1.
a - The schematic diagram of measurements of zinc
concentration in a bicrystal after diffusional anneal.
The trajectories of electron microprobe during
measurements of bulk and grain boundary diffusion
coefficients are presented.
b - The schematic diagram of measurement of a contact
angle at the site of grain boundary intersection with
the sample surface
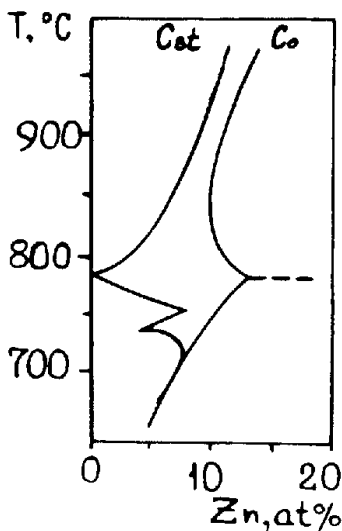
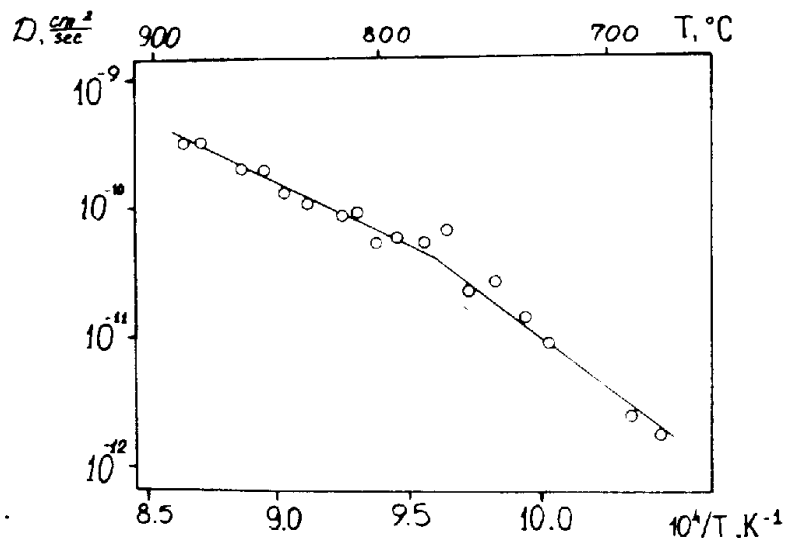c - Grain boundary and bulk phase diagram of the system
(Fe-5at.%Si)-Zn [1].

Fig.2. The temperature dependence
of the bulk diffusion coefficient
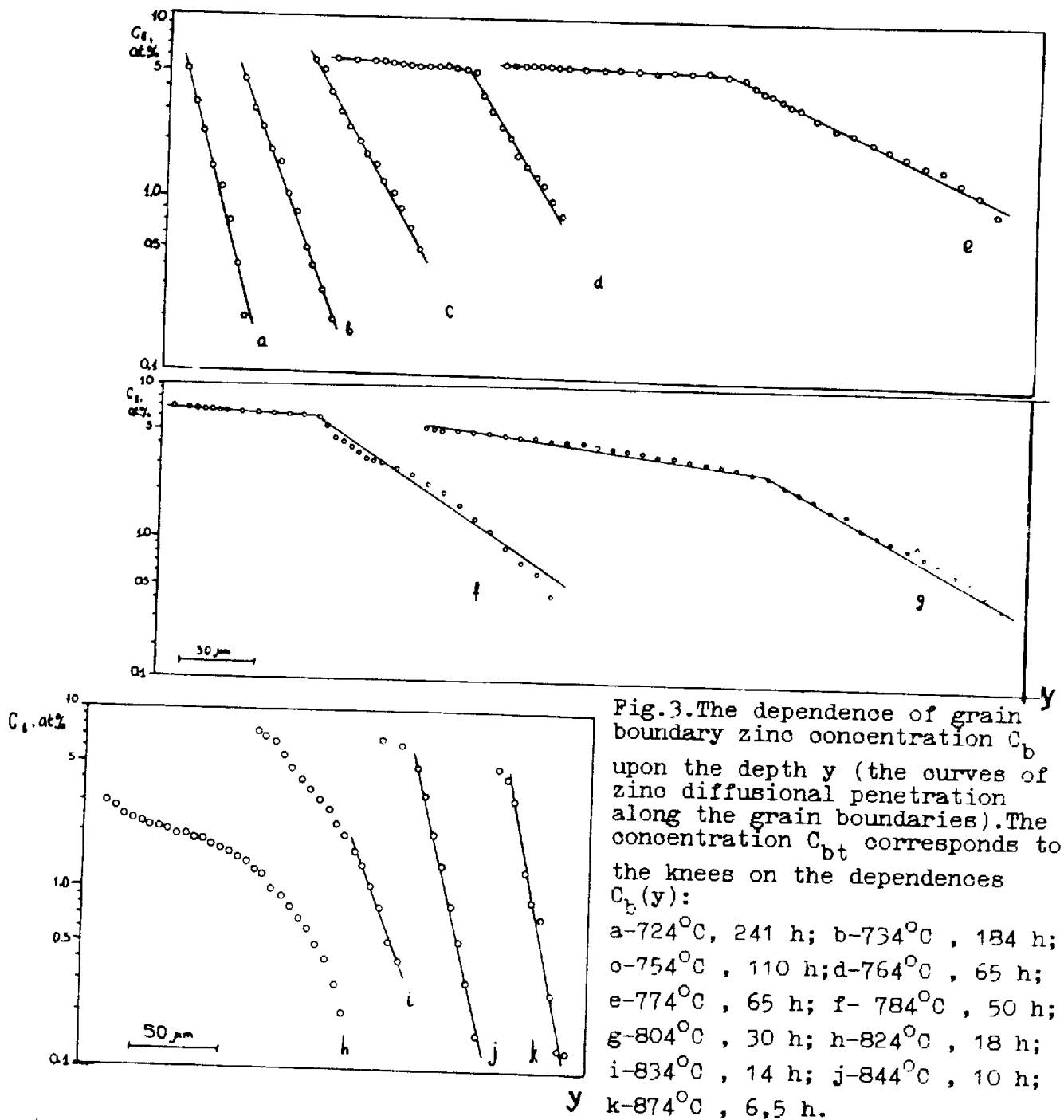D of zinc in the alloy Fe-12at.%Si.

Fig.3.The dependence of grain boundary zinc concentration C_b upon the depth y (the curves of zinc diffusional penetration along the grain boundaries).The concentration C_{bt} corresponds to the knees on the dependences $C_b(y)$:

a-724°C, 241 h; b-734°C , 184 h;

c-754°C , 110 h;d-764°C , 65 h;

e-774°C , 65 h; f- 784°C , 50 h;

g-804°C , 30 h; h-824°C , 18 h;

i-834°C , 14 h; j-844°C , 10 h;

k-874°C , 6,5 h.

The temperature was maintained with accuracy ±0.5°C. On the obtained samples, the zinc content distribution was determined by means of electron microprobe analysis (see fig.1). To determine the concentration by intensity of the characteristic X-ray radiation, the necessary corrections of the standard methods of quantitative electron microprobe analysis were introduced [7].

The value of product of the grain boundary diffusion coefficient D_b and the diffusion thickness of the grain boundary δ was determined using the Fisher's equation with the correction for concentrational dependence of the bulk diffusion coefficient D [8]:

$$D_b \delta = 2y^2 (D^o/\pi t)^{1/2} (1+2\beta C_o/3\pi)/(\log C_b/C_o)^2$$

Here, y is distance to sample surface, t-anneal duration, D^o and β are parameters.

Results

In fig.2,the temperature dependence of zinc bulk diffusion coefficient for the alloy Fe-12at.%Si is presented. It can be seen that the temperature dependence $D(T)$ consists of two regions with different slope. They intersect at about $770^{\circ}C$. This temperature is close to the A_2-B_2 ordering temperature in the alloy Fe-12at.%Si [6]. Above the ordering temperature T_{ord}, the activation energy of the bulk zinc diffusion E is 170 kJ/mole, below T_{ord}, E=324 kJ/mole.

In fig.4b, the temperature dependence of the angle θ at the site of intersection of grain boundary with the sample surface is presented (for determination of θ see the diagram in fig.1). At lower temperatures, the θ angle is nearly 180°. At the temperature $T_w = 749\pm4^{\circ}C$, the wetting transition occurs: above this temperature the grain bounbary is wettable by the Zn-based solution, which is formed due to melting of the surface layer of the diffusant during the anneal. In fig.3 the dependences of grain-boundary zinc concentration C_b upon the depth y (the curves of zinc diffusional penetration along the grain boundaries) are presented, while fig.5 displays the temperature dependences of value of the product $D_b\delta$. The grain boundary behavior can be seen to depend on the temperature strongly. Below the temperature T_w the dependence $C_b(y)$ contain a steep region only. Above the temperature T_w, there appears a gentle region (corresponding to high diffusivity) along with the steep one. The steep and gentle regions intersect at a concentration C_{bt}. Therefore, to each curve of zinc diffusional penetration along the grain boundaries $C_b(y)$ correspond two points in fig.5. The values of $D_b\delta$ for both gentle and steep parts of $C_b(y)$ increase drastically with the temperature and approach their maxima simultaneously at $774^{\circ}C$.

In the concentration range from C_o to C_{bt} the product $D_b\delta$ is 10-100 times more than at concentrations below C_{bt}. The transformation from the "usual" to accelerated grain-boundary diffusion occurs abruptly at concentration C_{bt}. At this concentration, a knee is observed on the curves of zinc diffusional penetration along the grain boundaries $C_b(y)$. The concentration C_{bt} was earlier shown to be an equilibrium parameter of the grain boundaries. In particular, it does not depend upon the annealing time. At a temperature above $T_{crit} = 809\pm4^{\circ}C$ the knees disappear from the dependences $C_b(y)$. In the interval of 30 - 40$^{\circ}C$ above the critical temperature T_{crit}, the curves $C_b(y)$ are essentially non-linear.They still contain traces of the gentle region. At the temperature above approximately $840^{\circ}C$, the curves contain only the steep region again. In the temperature range 774...840$^{\circ}C$ (beginning from the disordering temperature), the diffusion permeability of grain boundaries decreases strongly.

In fig.4a, the phase diagram is presented. White points indicate the values of the bulk solubility limit of zinc in the alloy Fe-12at.%Si (solvus line). Black points correspond to the values of concentration C_{bt}, at which the knees on the curves $C_b(y)$ are observed, and the diffusion permeability of the grain boundaries undergoes abrupt change. At the temperature T_w the wetting transition occurs.It can be clearly seen that the $C_{bt}(T)$ line unites with the solvus line $C_o(T)$ at the temperature T_w. Really, at this temperature the grain boundary wetting and gentle region on the zinc grain boundary diffusion curves $C_b(y)$ disappear simultaneously. Above T_w, the $C_b(T)$ line gradually goes away from the solvus line $C_o(T)$,and is ended by a critical point at $804^{\circ}C<T<814^{\circ}C$. At the temperature $804^{\circ}C$, the penetration curve $C_b(y)$ still contains a knee, while at T=810$^{\circ}C$ such knee is absent, although the penetration curve has some traces of steep and gentle regions (see fig.5). In

the vicinity of the bulk ordering temperature T_{ord} protrusions directed towards the region of low concentrations can be seen on the line C_{bt} (T) and the solvus line C_o(T).

Discussion

It is known that any ordering (spin, atomic, etc) always cause the increase of the diffusion activation energy (see e.g. [9,10,11]), including the grain-boundary diffusion [11]. Qualitatively it is quite understandable:
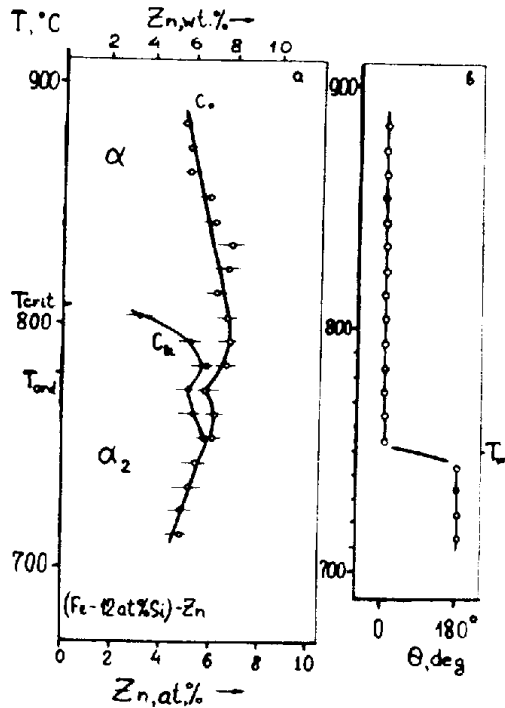

Fig.4 a.-Phase diagram of the system (Fe-12at.%Si)-Zn. T_{ord}-temperature of the bulk ordering A_2- B_2; T_{crit}- the critical point on the line C_{bt}(T) of grain boundary premelting transition
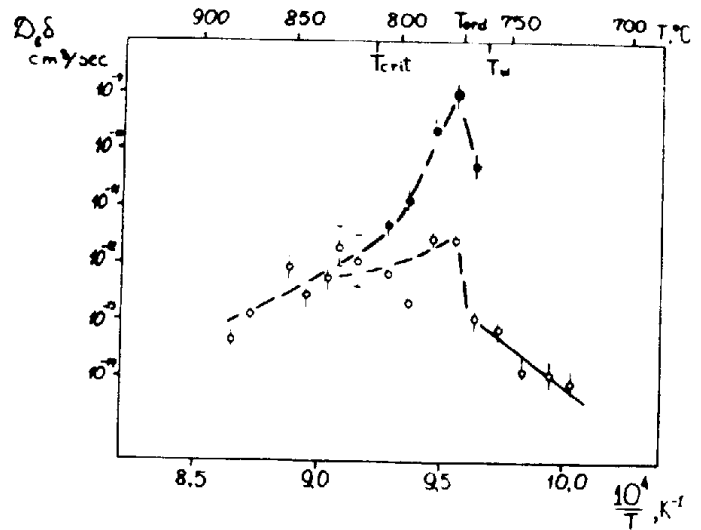

Fig.5 The temperature dependence of the value of product $D_b\delta$. Solid points correspond to concentration in range from C_o to C_{bt}.

b-Temperature dependence of the angle θ in site of the grain boundary intersection with the surface. T_w - temperature of grain boundary wetting transition

formation and migration of vacancies in an ordered alloy are connected with "breaking" of additional bonds. This contribution can be represented by an additional term in the activation energy of diffusion, roughly proportional to the square of the order parameter [13]. But the order parameter itself undergoes significant changes in the vicinity of the ordering temperature. This leads to strong temperature dependence and to high "effective" values of the activation energy. Really, the obtained value of the activation energy of bulk diffusion in the ordered state significantly exceeds usual parameters of iron and its alloys [14].

It is interesting that below the ordering temperature, at which the bulk diffusion activation energy grows abruptly, the grain boundary wetting also disappears. The transition from the disorded paramagnetic state into ordered ferromagnetic state (as was shown in the previous paper [1]) must suppress both wetting and the process of formation of thin equilibrium interlayers on grain boundaries (premelting, prewetting, etc.).

In the alloy Fe-12at.%Si we also see that above the temperature of wetting transition T_w a region of accelerated diffusion appears on the grain boundary in the concentration range from C_o to C_{bt}. Apparently we again deal with the same grain boundary premelting transition as in the alloy with lower silicon content. However, now the situation is more complex: we see first that the bulk ordering suppresses wetting and premelting on grain boundaries; second, the line of the premelting transition does not reach the region of high temperatures, as in [1], but is finished by a critical point. On the other hand, a protrusion directed towards low zinc content is observed on the line of premelting transition in the vicinity of the atomic ordering temperature T_{ord} , similar to that observed near Curie point T_o in [1]. A similar protrusion can be observed on the solvus line $C_o(T)$. Such protrusions are always formed when a line of second order phase transitions intersects a line of first order phase transitions [15].

Why does ordering suppress wetting and premelting on grain boundaries? A necessary (but not sufficient) condition of complete wetting is the relation $\sigma_{gb} > 2\sigma_{of}$,where σ_{gb} is the surface tension of a grain boundary, and σ_{of} is the surface tension of the interphase boundary "crystal - wetting phase".Ordering may be considered to be a process of formation of additional bonds between the atoms A and B. Wetting interlayer breaks all such bonds, while on the coincidence grain boundary they are partially conserved. Therefore, the contribution of ordering into $2\sigma_{of}$ is greater than into σ_{gb}.

In ref. [16] an anomalous behavior of diffusion coefficient directly near the phase transition is studied theoretically. We suppose that in our case we have observed something like that.

References

1. E.I.Rabkin, B.B.Straumal and L.S.Shvindlerman,J.de Physique Colloque, 51, C599 (1990)
2. L.S.Shvindlerman, W.Lojkowski, E.I.Rabkin and B.B.Straumal J.de Physique Colloque, 51, C629 (1990)
3. P.G.De Gennes, Rew.of Mod. Phys.57, 827 (1985).
4. S.Dietrich, in: "Phase Transittions and Critical Phenomena",ed.by C.Domb and J.Lebowitz, p.1-218, v.12, Academic Press, London (1988).
5. J.W.Cahn, J.Chem.Phys. 66, 3667 (1977).
6. O.Kubaschevski, Iron Binary Phase Diagrams, Springer-Verlag, Berlin etc.; Verlag Stanleisen m.b.h., Duesseldorf (1982).
7. S.J.B.Reed, Electron Microprobe Analysis, Cambridge University Press, Cambridge et al. (1975).
8. E.I.Rabkin, V.N.Semenov, B.B.Straumal, L.S.Shvindlerman, Acta Metall, to be published
9. Y.Funamizu and K.Watanabe, J.Jap.Inst.Met. 37, 1087 (1975).
10. L.Ruch, D.R.Sain, H.L.Yen ahd L.A.Girifalko, J.Phys.Chem Solids, 37, 649 (1976).
11. P.Moulin, A.M.Huntz and P.Lacombe, Acta Metall. 27,1431 (1979).
12. I.Kaur, W.Gust and L.Kozma, Handbook of Grain and Interphase Boundary Diffusion Data, Ziegler Press, Stuttgart (1989).
13. L.A.Girifalko, Statistical Physics of Materials, John Wiley and Sons, New-York et.al. (1973).
14. Metals Reference Book, Ed. by Smithels C.I., Butterworth, London (1976).
15. Alloy Phase Diagrams, eds. L.H.Bennett, T.B.Massalski and B.C.Giessen, North-Holland, New York et. al.,1983.
16. L.A.Bol'shov, M.S.Veshchunov, Sov.Phys.JETP, 95, 2039 (1989) (in Russian)