

# INVESTIGATION OF GRAPHITIZATION PROCESS OF ALLOYS Fe-C, Co-C, Ni-C, FeMe-C (Me = V, Cr Ti, Co, Ni)

*D.V. Schur<sup>a</sup>, Z.A. Matysina<sup>b</sup>, S.Yu. Zaginaichenko<sup>c</sup>*

*<sup>a</sup> Institute of Hydrogen and Solar Energy, P.O. Box 195, Kiev-150, 03150 Ukraine*

*<sup>b</sup> Dnepropetrovsk State University, Dnepropetrovsk, 49000 Ukraine*

*<sup>c</sup> Institute for Problems of Materials Science of NAS, Kiev, 03142 Ukraine*

## **Abstract**

A theoretical investigation of diffusion, distribution and thermally activated redistribution of carbon interstitial atoms C about the volume and surface both of crystalline films and massive crystals AB has been carried out. These crystals have bcc lattice and various types of free facets. The dependence of carbon filling of the surface and volume interstitial sites upon the films' temperature and composition have been studied.

Changing the temperature or pressure leads to the redistribution of C atoms in the system. The thermally activated processes of C-atom redistribution among the volumetric and surface film interstices in AB alloy are investigated. The formulae for the equilibrium concentrations of carbon interstitial atoms and the rate or relaxation time of interstitial atoms redistribution in dependence on concentrations of A, B alloy components, on long range order in A, B atoms distribution at the sites of crystal lattice, on temperature, on interaction energies of atomic pairs AC, BC are determined.

Theoretical calculations have been compared with experimental data on graphitization of Fe-C, Co-C, Ni-C, FeMe-C alloys, where Me = V, Cr, Ti, Co, Ni. The theory has been found to be in a satisfactory agreement with experiment on temperature dependence of carbon concentration in the volume of Fe-C, Co-C, Ni-C alloys.

## **Introduction**

The presence of the free surface in crystal can lead to a corresponding distribution of interstitial atoms (carbon, hydrogen) about the interstitial sites on the surface and in the crystal's volume. A change of the thermo-dynamic parameters, as temperature and pressure, leads to the redistribution of interstitial atoms in the system. Knowledge of these processes rates can prove to be important, for example, for the selection of heat treatment regimes for alloys. The surface segregation of interstitial atoms is used in practice for the obtaining of certain surface physical characteristics of crystals, for the prediction of material-making techniques of new chemical compositions.

This paper describes a theoretical investigation of the impurity distribution of interstitial C atoms on the surface and in the volume both of the films and massive crystals AB. The thermally activated processes of carbon interstitial atoms redistribution among the volumetric and surface film interstices are investigated theoretically and also results from the calculation of the dependences of the equilibrium concentrations of carbon in the film interstitial sites on the alloy composition, temperature, atomic order and energetic parameters of interatomic interaction are listed below.

### **Interstitial atoms at the volumetric and surface interstices**

The monomolecular model of the surface and the principle of detailed equilibration are used in

calculations. The subject of inquiry is the film of an ordering alloy AB with the body-centred cubic structure that consists of  $n$  atomic layers with two free surfaces. It is supposed that interstitial atoms C are located in interstitial sites of one type (e.g., octahedral) with the different coordination on the surface and in the volume, i.e. the film has the volumetric V and the surface S interstitial sites.

The temperature change from the value  $T_1$  to  $T_2$  disturbs the thermodynamic equilibrium and initiates the redistribution of C atoms. This theory includes the premise that the redistribution of slow A, B atoms does not take place at lattice sites. The solution of the kinetic equations for the  $V \rightleftharpoons S$  transitions shows the exponential dependence of  $\nu_V$ ,  $\nu_S$  concentrations of carbon interstitial atoms on time  $t$

$$\begin{aligned} \nu_V(t) &= \Delta\tilde{\nu}_V \exp\left(-\frac{t}{t_*}\right) + \tilde{\nu}_V(T_2), \\ \nu_S(t) &= \Delta\tilde{\nu}_S \exp\left(-\frac{t}{t_*}\right) + \tilde{\nu}_S(T_2), \end{aligned} \quad (1)$$

where

$$\tilde{\nu}_V(T) = \left[1 + \frac{1}{n} \exp\left(-\frac{v_S - v_V}{kT}\right)\right]^{-1}, \quad \tilde{\nu}_S(T) = \left[1 + n \exp\left(-\frac{v_V - v_S}{kT}\right)\right]^{-1} \quad (2)$$

are the equilibrium concentrations of interstitial atoms C at the V and S interstices;  $\Delta\tilde{\nu}_V = \tilde{\nu}_V(T_1) - \tilde{\nu}_V(T_2)$ ;  $\Delta\tilde{\nu}_S = \tilde{\nu}_S(T_1) - \tilde{\nu}_S(T_2)$  are the changes of equilibrium concentrations  $\tilde{\nu}_V$ ,  $\tilde{\nu}_S$  at the  $T_1 \rightarrow T_2$  temperature change,  $v_V$ ,  $v_S$  are the energies of C atom in the V and S interstices, which are dependent on the alloy structure and composition, atomic order and the  $v_{AC}$  and  $v_{BC}$  energetic parameters of the interatomic interaction of AC and BC pairs,  $v_B$  is the C atom energy in the vertex of potential barrier at the  $V \rightleftharpoons S$  transitions;

$$t_* = \frac{\tau}{4} \left[ \exp\left(-\frac{(v_V - v_B)}{kT}\right) + n \exp\left(-\frac{(v_S - v_B)}{kT}\right) \right]^{-1}, \quad (3)$$

$$\tau \approx 10^{-3} \text{ s}$$

is the relaxation time of the redistribution process of the interstitial atoms that escape the potential barrier  $v_B$  at the  $V \rightleftharpoons S$  transitions.

The  $\nu_V(t)$ ,  $\nu_S(t)$  dependences are monotonic functions in accordance with (1). The investigation of equations (1) show that plots (Fig. 1) of  $\nu_V(t)$  and  $\nu_S(t)$  dependences have a greater rate of change if  $\nu_V < \nu_S$  in comparison with the same if  $\nu_V > \nu_S$ . Therefore, from the curve slope one might suppose the value and the sign of energetic parameters  $v_V$ ,  $v_S$  and the kind of this dependence (strong or weak) dictates the interaction character of AC, BC pairs.

### Distribution of carbon interstitial atoms at the interstices of three types

In certain cases, i.e. when the nodal plane (111) is the free face, the potential surface of the crystal lattice provides two types of surface interstitial sites  $S_1$ ,  $S_2$  with a different depth of the potential well (Fig. 2). Kinetic equations permit the establishing of the time dependence of the  $\nu_V$ ,  $\nu_{S_1}$ ,  $\nu_{S_2}$  concentrations for the  $V \rightleftharpoons S_1$ ,  $V \rightleftharpoons S_2$ ,  $S_1 \rightleftharpoons S_2$  transitions and the extremal dependence of carbon atoms concentrations  $\nu_S(t)$  on time may be shown for interstitial sites with average depth of potential well (Fig. 3).

The extremal dependence of concentrations (Fig. 1) on time don't take place with a distribution of interstitial atoms only in interstitial sites of two types. Therefore, as a result of experiments the presence of a maximum at the dependence  $\nu_S(t)$  suggests the distribution of carbon interstitial atoms in interstitial sites of three types.

The equilibrium concentrations of interstitial atoms C, the rate or time of relaxation (3) of interstitial atoms redistribution are dependent on the  $a$ ,  $b$  concentrations of A, B alloy components, on the

long range order  $\eta$  in the A, B atoms distribution at the sites of crystal lattice and on the temperature T. These dependences may be elucidated if the dependences of  $v_V, v_S, v_B$  energies on  $a, b, \eta, T$  can be determined.

In the particular cases: 1)  $b = 0$ ; 2)  $b \ll 1$ ; 3)  $\eta = 0$ ; 4)  $\eta \ll 1$  the formulae for the relaxation time assume the forms

$$t_A^* = \frac{\tau}{4} \left( n \exp \frac{v_{AC}}{kT} + \exp \frac{v'_{AC}}{kT} \right)^{-1} \text{ if } b = 0, \quad (4)$$

$$t^* = t_A^* \left( 1 + b \frac{n \alpha \exp \frac{v_{AC} + v'_{AC}}{kT} - \beta}{n \exp \frac{v_{AC} + v'_{AC}}{kT}} \right) \text{ if } b \ll 1, \quad (5)$$

$$t_o^* = \frac{\tau}{4} \left( n \exp \frac{a v_{AC} + b v_{BC}}{kT} + \exp \frac{-a v'_{AC} - b v'_{BC}}{kT} \right)^{-1}, \quad (6)$$

if  $\eta = 0$

$$t^* = t_o^* \left[ 1 - \frac{1}{2} \eta \frac{3n(\alpha - 2\beta) \exp \frac{a v_{AC} + b v_{BC}}{kT} + (3\alpha - 7\beta) \exp \frac{-a v'_{AC} - b v'_{BC}}{kT}}{n \exp \frac{a v_{AC} + b v_{BC}}{kT} + \exp \frac{-a v'_{AC} - b v'_{BC}}{kT}} \right], \quad (7)$$

if  $\eta \ll 1$

where

$$\alpha = (v_{AC} - v_{BC})/kT, \quad \beta = (v'_{AC} - v'_{BC})/kT, \quad (8)$$

and the  $v_{AC}, v_{BC}, v'_{AC}, v'_{BC}$  are the interaction energies of atomic pairs AC, BC being correspondingly at the 0,5d and 0,7d distances, where d is the lattice parameter.

The formula (4) represents the relaxation time for the pure metal A. The formula (5) permits to ascertain the exerted influence of an impurity B to the metal A on the relaxation time and it follows from this dependence that the B impurity increases the time of relaxation and reduces the rate of redistribution of carbon atoms among the interstitial sites in the case of

$$n \alpha \exp \frac{v_{AC} + v'_{AC}}{kT} > \beta. \quad (9)$$

As appears from the above, doping and suitable selection of B component can change the relaxation time in the necessary direction.

The formula (6) defines the relaxation time of a disordered alloy AB of any composition. It follows from that formula that the dependence  $t_o^*(a)$  can have a maximum at the composition

$$a^* = \left[ \ln \frac{v'_{AC} - v'_{BC}}{n(v_{AC} - v_{BC})} - 1 \right] / \left( \frac{v_{AC} + v'_{AC}}{v_{BC} + v'_{BC}} - 1 \right). \quad (10)$$

The knowledge of the energetic parameters for each specific disordered alloy gives the possibility of selecting the interval of concentrations with the most suitable value of the relaxation time that can permit either the acceleration or the slowing down of the redistribution process of the interstitial atoms C along the film interstices.

The formula (7) permits the obtaining of more specific information about the influence of the long range order on the redistribution process of interstitial atoms C. It follows from (6) that atomic order  $\eta$  decreases the relaxation time and, consequently, speeds up the process of redistribution of interstitial atoms C under the conditions

$$3n(\alpha - 2\beta) \exp \frac{a(v_{AC} + v'_{AC}) + b(v_{BC} + v'_{BC})}{kT} > 4\alpha - 7\beta. \quad (11)$$

Knowledge of the energy parameters and the temperature (that must be below the Kurnakov temperature) permits the estimation of the influence of order on the relaxation time.

The formulae, determined the influence of B admixture to the metal A on the equilibrium concentrations of interstitial atoms C, at  $b \ll 1$  have a form

$$\begin{aligned}\tilde{v}_v(T) &= \tilde{v}_v^A [1 - b(\alpha + \beta)\tilde{v}_s^A], \\ \tilde{v}_s(T) &= \tilde{v}_s^A [1 + b(\alpha + \beta)\tilde{v}_v^A],\end{aligned}\quad (12)$$

where  $v_v^A$ ,  $v_s^A$  are the such concentrations for metal A. As is obvious from (12), the B admixture decreases the volumetric concentration  $v_v$  and increases the surface concentration  $v_s$  of interstitial atoms C under condition  $\alpha + \beta > 0$ . Therefore, one can regulate the process of segregation and liquation by addition and selection of B admixture.

Thus, if the values of energetic parameters for each alloy are known from independent experiments, for example, by the estimated values of the diffusion activation energies, then by means of formulae (4)-(7) one can predetermine the influence of composition, atomic order and temperature on the value of the equilibrium concentration of carbon interstitial atoms and the relaxation time for the process of temperature redistribution of C atoms among the interstices in AB alloy. By suitable selection of alloy composition and specific atomic order in it (by means of thermal annealing), one can purposefully change the  $t^*$  value with a view to attain equilibrium quickly or, on the contrary, to freeze a definite non-equilibrium state. And that in turn will exert an influence equally upon the forming of one or another physical and chemical properties of the alloy.

Theoretical results for equilibrium concentrations (2), (12) of interstitial atoms, for the kinetic curves (1) and for the relaxation time (4)-(7) have been

compared with experimental data concerning the graphitization of Fe-C, Co-C, Ni-C alloys and Fe-C alloy with the addition of Cr, V, Co, Ni, Ti metals [8] (see Fig. 4). In the paper [8] the temperatures of graphitization onset have been defined experimentally for different carbon concentrations in Fe-C, Co-C and Ni-C alloys. These data allow the determination of volumetric carbon concentration  $\tilde{v}_v(T)$  for different temperatures of alloys. Solid circles of Fig. 4 show these experimental results.

A knowledge of diffusion activation energies of interstitial atoms allow the evaluation of energetic parameters entered into theoretical equations. For example, with the assumption of diffusion by the vacancy mechanism we have for A-C alloy

$$v_v - v_s = v_{AC} = -Q, \quad (14)$$

where Q is the diffusion activation energy of interstitial atoms. In this case curves of Fig. 4 plotted by formula (2) for  $n = 10^3$  show satisfactory agreement of theory and experimental data.

The dispersion of the experimental points on the Fig. 4 is conditioned by variation of the rate  $v$  of specimen cooling in evaluating the temperature T of graphitization onset. At high rate  $v$  the graphitization onset temperature nonequilibrium, it has a conservative value. Its dependence on the rate of specimen cooling  $T(v)$  characterize the kinetics of carbon atoms redistribution along the volumetric and the surface interstitial sites of alloy. The plots of this dependence are illustrated in Fig. 5.

The experimental plots  $T(v)$  of Fig. 5 can be correlated with the theoretical plots  $v_i(t)$  of Fig. 1 and 3. Really for prolonged length of time t and small rate of cooling  $v$  the equilibrium state is established in alloy, i.e. the equilibrium concentrations of interstitial atoms in the volume and at the surface are fixed. But for small time periods t and respectively high rate  $v$  the state of

alloy will be yet non-equilibrium. It is in this range of high concentrations of interstitial impurity, when carbon atoms are located in the interstitial sites of different type, the extreme properties of alloy can be manifested, i.e. the dependences  $v_i(t)$  and  $T(v)$  can be ambiguous, the extremum can be found on the curves of these dependences. We observe minimums on experimental curves 1 and 3 of Fig. 5 at the rate of  $v \approx 130$  K/min. The minimum disappears with decreasing carbon concentration from  $c = 3,09$  at.% to  $1,96$  at.%. The comparison of calculated and experimental kinetic curves of graphitization process permits the statement that presence of minimum at these curves for Co-C and Fe-C alloys points out the distribution of carbon atoms in interstitial sites of different type.

### Conclusions

The comparison of theoretical and experimental plots for the volume concentration of carbon in Co-C, Fe-C, Ni-C demonstrate that the relationship between activation energies corresponds to data of independent experiments, i.e.  $Q_{Ni} > Q_{Co} > Q_{Fe}$ . In this case the values of activation energies are low in comparison with experiments [5-7], but our  $Q$  values are closer to experiment than in the paper [8].

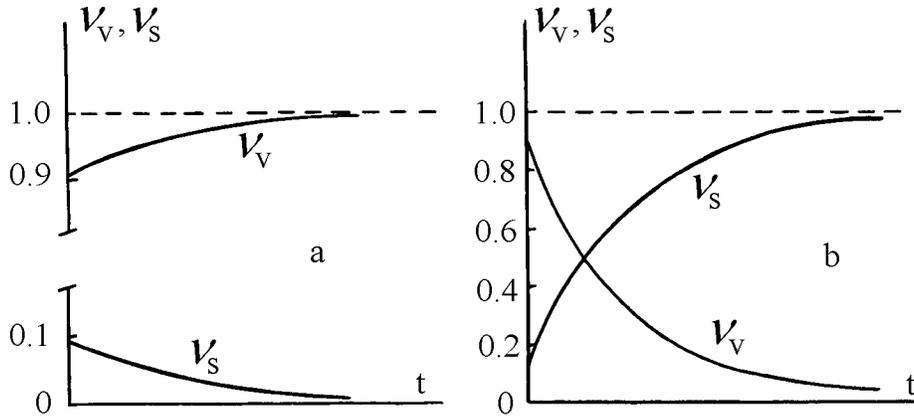
Furthermore, as  $Q_V < Q_{Cr} < Q_{Fe} < Q_{Ti} < Q_{Co} < Q_{Ni}$ , then by our calculations V or Cr addition to Fe must decrease the surface concentration of carbon, but Ti, Co or Ni impurity must increase it. This conclusion is in complete agreement with experimental results: it is well known that addition of V or Cr to Fe inhibit and of Ti, Co or Ni to Fe accelerate the graphitization of FeMe-C alloys, where Me=H, Cr, Ti, Co, Ni [4].

The presented dependences for the equilibrium concentrations of impurity and the relaxation on time of redistribution of impurity atoms can be

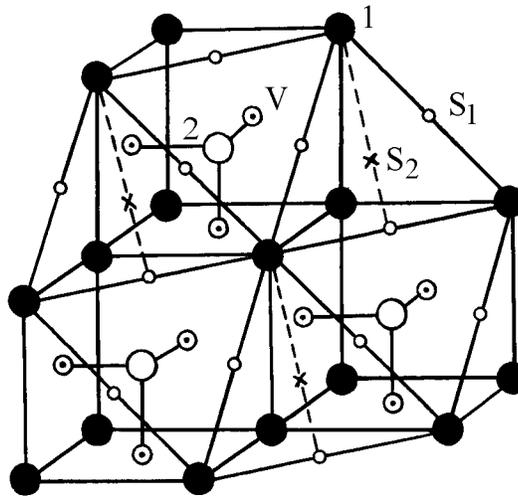
used for creation of polycrystalline films with resistant surface properties conserved in a wide temperature range.

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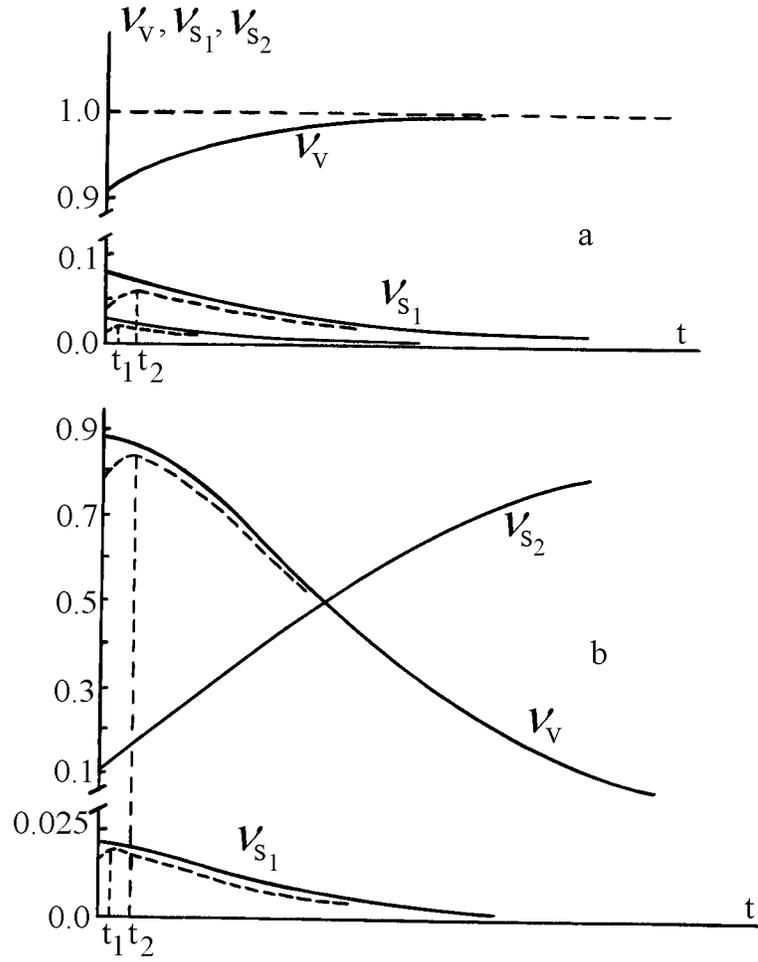
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**Fig. 1.** Time dependence of concentrations of interstitial atoms in interstices of two types V, S in response to a sharp temperature decrease of metal thin film ( $n=10$ )  
 a) attraction character of interacting forces of atomic pairs AC ( $v_V > v_S$ ),  
 b) repulsion character of interacting forces of atomic pairs AC ( $v_V < v_S$ ).

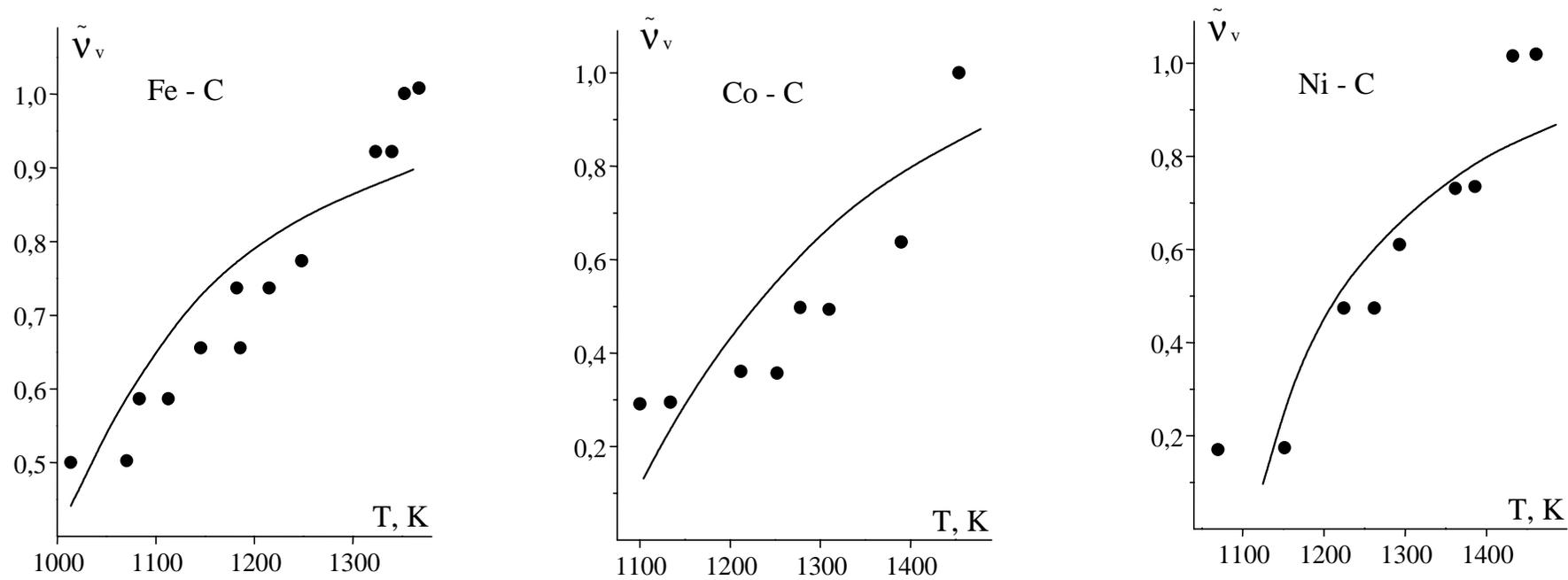


**Fig. 2.** Face (111) of crystal with bcc structure and upper surface layer  
 ● - sites of first type, ○ - sites of second type,  
 ⊙ - volume interstices V, ○, × - surface interstices  $S_1, S_2$ .

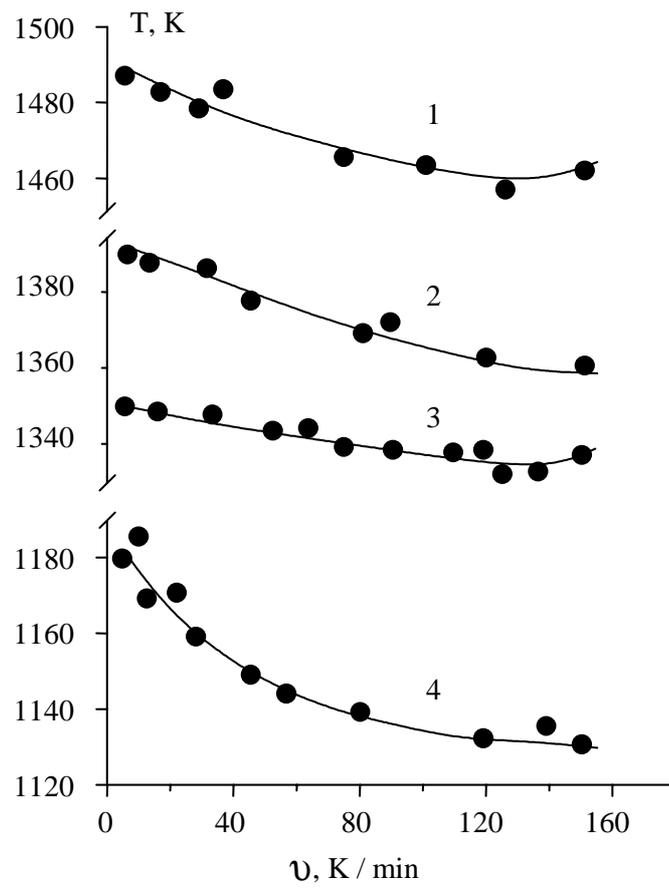


**Fig. 3.** Possible view of time dependences of interstitial atoms concentrations in interstices of three types V, S<sub>1</sub>, S<sub>2</sub> in response to a sharp temperature decrease of metal thin film (n=10). Dotted lines show these dependences in presence of maximum.

- a) interacting forces of atomic pairs AC have attraction nature ( $v_V > v_{S_1} > v_{S_2}$ ),
- b) interacting forces of atomic pairs AC have repulsion nature ( $v_V < v_{S_1} < v_{S_2}$ ).



**Fig. 4.** Curves of the temperature dependence of the equilibrium concentration of carbon atoms in the volume of Fe-C, Co-C, Ni-C alloys. Solid circles correspond to experimental data [8], curves – to theoretical calculations.



**Fig. 5.** Experimental plots of the temperature of graphitization onset as a function of the rate of alloys cooling: 1) Co-C with 3,09 at.% C, 2) Co-C with 1,96 at.% C, 3) Fe-C with 8,09 at.% C, 4) Ni-C with 1,12 at.% C.