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Calculation of Diffusivities in Ordering f.c.c. Alloy by the Kinetic Data about Short- and Long-Range Order Parameters' Relaxation

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1. Introduction

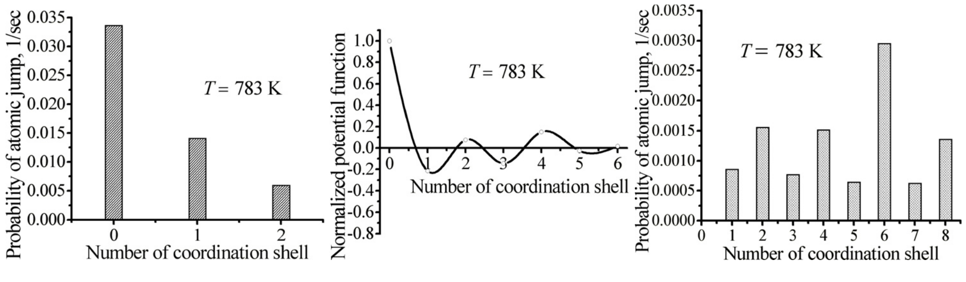
Short-range order is a unique natural phenomenon occurring by concentration heterogeneity, whose dimensions are commensurate with lattice parameters of the disordered alloy. Kinetics of short-range order is determined by the microscopic diffusion over intersite distances. Therefore, kinetic measurements of its relaxation provide us with more detailed information on the discrete diffusion mechanism such as a possibility to determine the microscopic characteristics of atomic migrations, including probabilities and types of atomic jumps, and activation energy of diffusion. Discrete diffusion measurements can be performed at room temperatures, because of the sufficiently short time scale of elementary diffusion events. It means that results can be utilized to determine the low-temperature diffusivities and activation energies.

2. Results

Considering an example of disordered $^{62}Ni_{0.765}Fe_{0.235}$ alloy, Khachaturyan's microscopic approach is used to study the elementary diffusion events in f.c.c. alloy.

Using available experimental data about diffuse-scattering kinetics in $^{62}Ni_{0.765}Fe_{0.235}$ [1], which is caused by short-range ordering in this alloy, the atomic jump probabilities are estimated.

For the 'ideal' $^{62}Ni_{0.765}Fe_{0.235}$ alloy atomic jump probabilities at a given site **R** from the nearest-neighbour sites and the next-nearest-neighbour sites are presented on Fig. 1a. Values of these probabilities stand for the predominance of atomic jumps within the first



(a) (b) (c)

Fig. 1: Atomic jump probabilities per unit time (a, c) and normalized potential function (b) in ideal (a) and non-ideal (b, c) $^{62}Ni_{0.765}Fe_{0.235}$ alloy.

coordination shell mainly by the vacancy of diffusion mechanism.

The dependence of the normalized 'potential' function of concentration heterogeneities at the 'zero' site on the radius of coordination shell, R_n, is non-monotonic (see Fig. 1b). For some R_n the function is positive, for another one—negative. This fact determines thermodynamic 'disadvantage' or 'advantage' of a given atom to stay on the corresponding sites $\{\mathbf{R}_n\}$.

In a non-ideal $^{62}Ni_{0.765}Fe_{0.235}$ alloy, the jump probability of a given atom into the site **R** in a potential field caused by the microscopic concentration heterogeneity is determined by the value of this field at site **R**. So, jumps' probability of atoms into the site **R** is non-monotonic (see Fig. 1c): it is higher for the sites, where the arrangement of a given atom is more energy-wise preferable.

In the presence of the $L1_2$-type order, Fe atoms try to occupy predominantly the cube corners and Ni atoms—face centres of cubic unit cells of f.c.c. lattice. Short-range order is characterised by the location of Fe atoms at the cube corners (sites within the coordination shells II, IV, VI, VIII)—they are more energy-wise preferable. Therefore, jump probabilities of Fe atoms into the sites $\mathbf{R}_{II}$, $\mathbf{R}_{IV}$, $\mathbf{R}_{VI}$, $\mathbf{R}_{VIII}$ (see Fig. 1c) are higher than jump probabilities at the centres of faces (sites $\mathbf{R}_{I}$, $\mathbf{R}_{III}$, $\mathbf{R}_{V}$, $\mathbf{R}_{VII}$).

Atomic jump probabilities enabled to calculate macroscopic diffusion characteristics, diffusion, D, and self-diffusion, D^*, coefficients of Fe atoms in $^{62}Ni_{0.765}Fe_{0.235}$: for 776 K $D = 4.49\cdot10^{-17}$ cm^2/sec, $D^* = 1.81\cdot10^{-17}$ cm^2/sec; for 783 K $D = 6.90\cdot10^{-17}$ cm^2/sec, $D^* = 2.55\cdot10^{-17}$ cm^2/sec. Total activation energies of diffusion and self-diffusion of Fe atoms were also evaluated: 2.13 eV and 3.47 eV, respectively.

The case of the exchange ('ring') diffusion mechanism in ordered Ni_3Fe alloy at temperatures below the temperature of order–disorder phase transition is also considered. Within the framework of a mean-field approach and the superposition of the static concentration waves a kinetic equation for the long-range order parameter is obtained. Using experimental data about the time dependence of long-range order parameters [2], average diffusive mobilities of Fe atoms in Ni_3Fe alloy are calculated: $\langle D^0\rangle \approx 1.03\cdot10^{-22}$ cm^2/sec for $T = 673$ K and $\langle D^0\rangle \approx 1.78\cdot10^{-22}$ cm^2/sec for $T = 743$ K. The estimated diffusion migration energy of Fe atoms (in a model without vacancies) is 0.34 eV. The vacancy formation energy in a former model is 84–90% of the total activation energy.

3. Conclusion

Obtained results show the possibility of evaluating 'macrodiffusivities' by means of 'microdiffusivities' from the independent data of short- and long-range order kinetics. The exchange (ring) diffusion mechanism in f.c.c.-Ni–Fe has a small probability. One can use the present scheme to determine the type of atomic ordering. The model can be used for multicomponent systems based on f.c.c. lattices as well.

References

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