FROM THE HISTORY OF PHYSICS

Ascending diffusion and the diffusion aftereffect

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The history of the discovery and investigation of ascending diffusion and the diffusion aftereffect is described. The role of V. S. Gorskiĭ (1905–1941) in the discovery and study of these effects is discussed. A brief presentation of V. S. Gorskiĭ's biography and the content of his pioneering work (1934–1935) on this problem is given. Diffusion inelasticity and equilibrium segregation are discussed within the framework of V. S. Gorskiĭ's ideas. Kinetic segregation, which appears in situations when an alloy contains an active source of vacancies and the diffusion of the components of the alloy is directly proportional to the different partial diffusion coefficients is discussed in the concluding section.

INTRODUCTION

It is well known that the diffusion of impurity atoms in a crystal is described by Fick's equation $\mathbf{J} = -D\nabla c/\omega$ (D is the diffusion coefficient, c is the dimensionless concentration, and ω is the atomic volume). The diffusing atoms are located in symmetric potential wells, and each atom hops in opposite directions with equal probability. The directed spreading of the atoms is a consequence of the entropic tendency for the atoms to become uniformly distributed over the volume of the crystal matrix.

The situation changes when a force field, external or internal relative to the crystal and determining the force $\mathbf{F}_g$ acting on the diffusing atoms, is present. This force field causes the potential barrier to become asymmetric, and a directed drifting of atoms should therefore be observed against the background of the Fick entropic migration. In this case the flux is determined by the equation

$$\mathbf{J} = -(D\nabla c - \zeta c \mathbf{F}_g)\,\omega^{-1}, \tag{1}$$

where the drifting of the atoms is described by the second term. In Eq. (1) $\zeta = D/kT$ is the mobility of the atoms.

The force $\mathbf{F}_g$ can, generally speaking, be produced by different fields—elastic-stress, thermal, electric, and vacancy fields. If ∇c and $\mathbf{F}_g$ are antiparallel, then $\mathbf{F}_g$ contributes to the diffusion of atoms an "ascending" diffusion component, directed opposite to ∇c and therefore acting not in the direction of leveling the distribution, but rather of segregating the impurity atoms. Thus ascending diffusion and diffusion segregation are interrelated effects.

In what follows we shall be discussing primarily the situation when the diffusion is affected by the elastic-stress field; the study of precisely this aspect of the problem aided in the discovery of many effects accompanying the diffusion of different types of atoms in crystals. We shall be interested primarily in diffusion effects determined by the effect of the elastic stress field on the diffusion of atoms: the effect of ascending diffusion itself, which accompanies the diffusion aftereffect, and diffusion segregation, V. S. Gorskiĭ, to whom this paper is dedicated, is known largely for his work on these effects.

In this paper we shall present Gorskiĭ's ideas and follow their subsequent development, in the course of which the link to Gorskiĭ's name was often lost.

V. S. GORSKIĬ'S BIOGRAPHY

For the problem under discussion the year 1985 is a double-anniversary year: Vadim Sergeevich Gorskiĭ (1905–1941), a well-known Soviet metal physicist and author of the first fundamental study on the problem of "ascending diffusion" was born 80 years ago and his paper "Theory of the elastic aftereffect in disordered solid solutions (elastic aftereffect of the second kind)," devoted to ascending diffusion and the diffusion aftereffect,[1] appeared in the journal Physikalische Zeitschrift der Sowjetunion 50 years ago (August 1935). During the last 50 years the ideas formulated and developed in this work were by no means ignored. These ideas are alive even today in the physics of real crystals and significantly affect many areas of this field.

We shall give a brief biography of Vadim Sergeevich Gorskiĭ. His life was unfortunately short and his interests single-minded. He was completely devoted to the physics of real crystals.

He was born in 1905 in Gatchina, near Leningrad, into the family of a railroad engineer. In 1926 he graduated from the Physico-mechanical Department of the Leningrad Polytechnic Institute—the main source of trained physicists of A. F. Ioffe's school.

In the mid-1920s as a student in Leningrad Gorskiĭ was an active participant of the famous seminar of "boys and girls," lovingly directed by its organizer Paul Sigizmund Ehrenfest (Fig. 1). V. S. Gorskiĭ also attended Ya. I. Frenkel's seminar.

V. S. Gorskiĭ began his scientific career while he was still a student, and already in 1928 he published in the Zeitschrift für Physik an exhaustive paper[2] on an x-ray diffraction study of ordered Cu–Au alloys, which was a presentation of his student thesis work.

In this paper, discussing the results of his x-ray diffraction experiments with Cu–Au alloys, V. S. Gorskiĭ first proposed a microscopic approach to the description of ordering in alloys, which substantially determined the further development of the well-known Gorskiĭ-Bragg-Williams theory

FIG. 1. Participants of P. S. Ehrenfest's seminar (Leningrad, 1924) (left to right): P. S. Ehrenfest, A. N. Arsen'eva, B. M. Gokhbertg, N. V. Tomashevskiĭ, P. O. Usataya, B. Ya. Pines, N. A. Brilliantov, A. I. Shal'nikov, and V. S. Gorskiĭ.

of ordering[2-4] (discussed in greater detail in Ref. 5).

At the beginning of 1930 V. S. Gorskiĭ arrived as an envoy from the Leningrad Physicotechnical Institute in Khar'kov, at the Ukrainian Physicotechnical Institute (UFTI) created under the initiative of A. F. Ioffe. The group arriving from Leningrad included many individuals who made a significant contribution to the development of Soviet physics: A. K. Val'ter, D. D. Ivanenko, A. I. Leĭpunskiĭ, I. V. Obreimov, and K. D. Sinel'nikov. They were soon joined by L. D. Landau and L. V. Shubnikov. A group of young researchers, actively working in the physics of crystals, including N. A. Brilliantov, R. I. Garber, and A. F. Prikhot'ko (Fig. 2), formed around I. V. Obreimov. They formed the creative atmosphere in which Gorskiĭ, as the organizer of the x-ray laboratory at UFTI, one of the few x-ray laboratories in the country at that time, developed his talent and performed his creative work.

He became a close friend of L. D. Landau. In his papers V. S. Gorskiĭ reports that he discussed with L. D. Landau a problem which he was studying and Landau helped him to construct a theory. He interacted equally actively with both theoreticians and experimentalists. V. S. Gorskiĭ, as the older and more experienced scientist, strongly influenced the creative character of the future academician L. F. Vereshchagin, as attested to by friends of theirs who are still alive.

Gorskiĭ's main work consisted of a deep investigation of ordering–disordering process in Cu–Au alloys. The effect of ascending diffusion and of the diffusion aftereffect, discussed below, were understood and discovered precisely in these works.

THE DIFFUSION AFTEREFFECT (INELASTICITY)

In studying ordering-disordering processes on the example of the binary compound Cu–Au,[1] V. S. Gorskiĭ pointed out the fact that since the elementary act of disordering (the interchange of the positions of two different neighboring atoms as a result of which both atoms are in the "wrong" positions) is accompanied by local deformation, an externally applied stress σ must bring about a change in the degree of disorder β. This deformation is a consequence of a jump in the volume, which in the presence of ordering accompanies the transition of the cubic lattice (disordered solution) into a tetragonal lattice (ordered structure).

The analysis[6] of the problem of the dependence of β on σ leads to the formula

FIG. 2. In the x-ray laboratory at UFTI (Khar'kov, 1924) (left to right): V. S. Gorskiĭ, I. V. Obreimov, R. I. Garber, and N. A. Brilliantov (published for the first time).

$$\frac{\Delta\beta}{\beta_\infty} \approx (1 - \beta_\infty) \frac{d\varepsilon}{d\beta} \frac{\widetilde{\omega}\sigma}{kT} ; \qquad (2)$$

where $\Delta\beta = \beta - \beta_\infty$, β_∞ is the degree of disorder in the absence of stress, $d\varepsilon/d\beta$ is the derivative of the deformation with respect to the degree of disorder in the presence of constant stress, $\varepsilon = (\omega_A - \omega_B)/\widetilde{\omega}$ is the dimensionless deformation accompanying the interchange of an atom of one type in a given position by an atom of another type, $\widetilde{\omega}$ is the effective atomic volume in the solution, and ω_A and ω_B are the volumes of the atoms A and B.

The degree of disorder β, corresponding to a given value of σ, must be established by means of a sequence of diffusion hops of atoms into the "wrong" positions. This means that the deformation accompanying this process should be observed in addition to the usual elastic (Hooke) deformation. The total deformation of a sample of unit length in the direction of action of the stresses must be represented in the form of two terms $\varepsilon = \varepsilon_{elas} + \varepsilon_{dif}$, where the elastic deformation $\varepsilon_{elas} = \sigma/E$ and the diffusion deformation $\varepsilon_{dif} = \Delta\beta(d\varepsilon/d\beta)$ (E is the modulus of elasticity). The dilatation of the sample owing to elastic and diffusion deformations in the process of loading and unloading is shown schematically in Fig. 3, where the characteristic relaxation time, measured from the moment of application and removal of the load, is denoted by τ.

The term ε_{dif} describes the deformation arising because of the change in the disorder. It is not a single-valued function of the stress, and for a fixed stress increases with time. This is determined by the fact that the spatial distribution of the atoms corresponding to a given degree β, as already mentioned, is formed in a diffusive manner. It is for this reason that this type of deformation is often called, following Zener,[7] diffusion inelasticity.

We emphasize that we are talking about deformation that does not obey the laws of the theory of elasticity and is not a single-valued function of the stress but rather an increasing function of time owing to relaxation of some indicators of nonequilibrium. In our case this is the degree of disorder.

Using the formula (2) and the definition of the quantities ε_{dif} and ε_{el} the ratio $\lambda = \varepsilon_{dif}/\varepsilon_{elas}$ can be put into the form

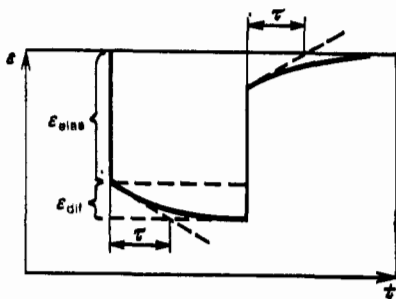$$\lambda = \beta_\infty (1 - \beta_\infty) \left(\frac{d\varepsilon}{d\beta} \right)^2 \frac{\widetilde{\omega}E}{kT} . \qquad (3)$$

For reasonable values of the constants ($\beta = 3 \cdot 10^{-1}$, $|d\varepsilon/d\beta| = 10^{-1}$)[14] it turns out that $\lambda = 4 \cdot 10^{-1}$ (see below).

V. S. Gorskiĭ investigated all the considerations presented above, the estimates, and the predictions[6,8] experimentally[8] in experiments in which with the help of an accurate dilatometric procedure he studied the deformation of a thin plate of Cu–Au under bending stresses, which could be applied and removed instantaneously (loading and unloading cycles). The typical dilatometric curves obtained in these experiments ($T = 227$–$370°$ C) are shown in Fig. 4, which shows both cycles.

In Gorskiĭ's experiments, performed under both loading and unloading conditions, the deformation ε_{dif} was observed clearly, and its rate increased with the temperature; the value of the ratio λ was reasonable. The reversibility of the deformation—both the Hooke deformation (which is trivial) and the diffusion deformation (which is predicted by the diffusion interpretation of the effect)—was of fundamental importance for the confirmation of the interpretation of the effect given above.

Gorskiĭ called the diffusion deformation effect which he discovered under conditions of variable degree of order in an ordered structure the "elastic aftereffect," Zener's term "diffusion inelasticity" became firmly established after the generality of V. S. Gorskiĭ's observations was discovered. The "aftereffect" which he studied was observed not only in ordered solid substitution solutions, but also in many other
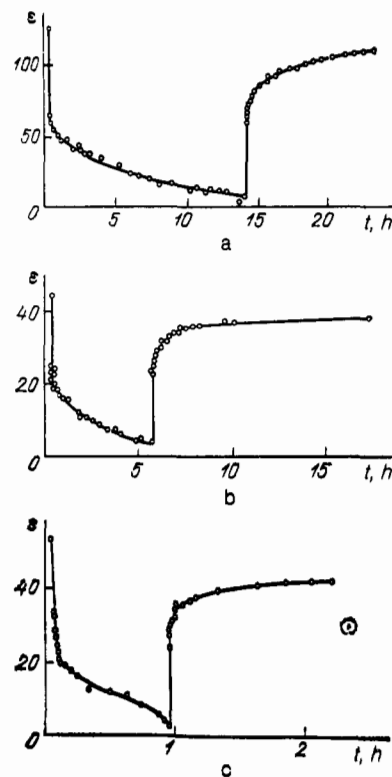

FIG. 4. Curves of deformation of a sample of a Cu–Au alloy with the application and removal of a load.[8] a) $T = 227$ °C; b) $T = 307$ °C; c) $T = 370$ °C.

FIG. 3. Elastic and diffusion deformation, observed with the application and removal of a load.

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objects, in particular, in solid interstitial solutions, and elsewhere.

As a widely known example of diffusion inelasticity, unrelated to ordering of a two-component solid substitution solution of the type AB, we call attention to the inelasticity appearing in solid interstitial solutions based on a metal with a body-centered cubic lattice. In this lattice (for example, α iron) the interstitial atom (for example, carbon) creates an anisotropic deformation. In addition, the displacement of the atom into a neighboring interstitial position is accompanied by a change in the direction of largest deformation. This indicates that an externally applied force will facilitate diffusion hopping of interstitial atoms, determining thereby their "ordering" and the accompanying inelastic deformation (see Ref. 9). The dilatometric effect observed during elastic loading and unloading of a sample of solid interstitial solution, is qualitatively similar to that observed by Gorskiĭ in experiments with Cu–Au samples.

It should be emphasized that two substantially different relaxation situations can occur. One situation is associated with relaxation of the internal order parameter. In particular, it is realized in experiments with ordered alloys of the type Cu–Au or interstitial solutions of the type αFe–C. In these cases the characteristic diffusion length is close to the interatomic distance.

A different situation is observed when the relaxation is associated with the change in the concentration distribution in the field of stresses varying over characteristic distances substantially exceeding the interatomic distance (the size of the sample, size of a separate grain, etc.). It is precisely this situation, in particular, that can be realized in disordered solid substitution solutions.

Since deformation in the presence of diffusion inelasticity is determined by elementary diffusion acts, data on the characteristic relaxation time τ should carry information on the coefficient of diffusion of atoms of the dissolved material in the crystal matrix. Indeed, from the time dependence of ε_{dif} it is possible to determine τ in the process under discussion. In the case when the characteristic diffusion length is close to the interatomic distance, the relationship between D and τ can be found by employing the well-known formula from the theory of random walk $D = \Gamma a^2/6$, where Γ is the hopping frequency and a is the hopping length of an atom. For a body-centered cubic lattice, which is the basis of the solid interstitial solution, it turns out that[9] $\Gamma = (2/3)\tau^{-1}$, $a = a_0/2$ (a_0 is the lattice parameter).

In the case when the characteristic diffusion length is of the order of the size of the sample, for example, equal to the diameter of the cylindrical sample d, it turns out[25] that $D = 7.38 \cdot 10^{-2} d^2/\tau$.

Very small values of D can be measured by the above-described method for determining the diffusion coefficient, which is based on the phenomenon of the elastic aftereffect. Reliably measured values of τ from 10 to 10^4 s correspond to values of D from 10^{-22} cm^2/s to 10^{-18} cm^2/s. Existing methods based on the use of Fick's law cannot provide the accuracy required for this.

There are a large number of measurements[26,27] in which the diffusion inelasticity effect discovered by V. S. Gorskiĭ

was used to obtain information on diffusion constants of hydrogen dissolved in vanadium, tantalum, niobium, etc.

As is well known,[28] resonance methods for measuring diffusion constants are based on the diffusion inelasticity effect. These methods are based on the fact that the maximum losses accompanying diffusion internal friction owing to the mismatch in the strain and deformation phases, caused by diffusion inelasticity, is observed when $\nu\tau \approx 1$ (ν is the frequency of application of the alternating stress). In particular, the diffusion constants of hydrogen and deuterium in tantalum were found from data on diffusion internal friction.[29]

EQUILIBRIUM SEGREGATION

By the begining of the 1930s there already existed separate experimental facts indicating that solid substitution and interstitial solutions do not behave like pure metals under deformation and subsequent annealing. Thus, for example, binary solutions under otherwise equal conditions exhibited under deformation a substantially higher mechanical hardening than pure metals. This refers also to the increment to the resistivity, which in solutions substantially exceeds the increment to the resistivity in pure metals; it was also accidentally discovered that in some deformed alloys annealing also increases the rupture strength and the hardness, i.e., their behavior is opposite to that of deformed pure metals. Under prolonged isothermal annealings, however, the mechanical characteristics were also observed to decrease after their unpredicted increase.

These "anomalies" in the behavior of the solutions could be, in any case, qualitatively, linked to the possible ascending diffusion fluxes, giving rise to local redistribution of the components of the solutions—a process which does not occur in pure metals. This is precisely what Gorskiĭ did in Ref. 1. Prior to Gorskiĭ, it was believed that the anomalies are a direct consequence of the nonuniformity of plastic deformation in the sample.

In the 1930s the possibility of the existence of partial fluxes of atoms of different types and partial vacancy fluxes was for all practical purposes ignored in the study of diffusion processes in solid solutions. These flows were considered primarily after the appearance of the well-known works by Smigelskas and Kirkendall[10] and Darken.[11] Before the appearance of these works, as believed at that time, the only factor capable of giving rise to diffusion redistribution of components was the fact that it is energetically favorable for atoms having a large atomic volume in a nonuniformly deformed region to move into a stretched region, while for atoms having a small atomic volume it is more favorable to move into a compressed region (Fig. 5). It is in this sense
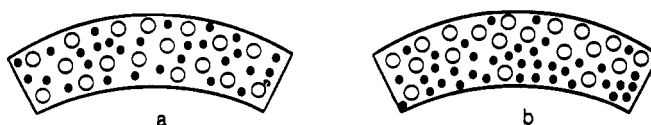

FIG. 5. Diagram of equilibrium segregation. a) After bending before annealing; b) after annealing.

that the difference in the atomic volumes can cause the diffusion redistribution of atoms of the solution in the state of ascending diffusion, in which segregated regions, enriched with atoms of different types, form. This process is facilitated by a drop in the energy of the system, and there is a basis for calling it equilibrium segregation, which forms under conditions of ascending diffusion. There is an analogy between equilibrium segregation in solutions in an elastic-stress field and the formation of a "barometric" distribution of a mixture of gases in a gravitational field.

Equilibrium diffusion segregation in the variant under discussion has the peculiarity that the reverse flow, which levels the concentration nonuniformity formed during ascending diffusion, is forbidden, since it must be accompanied by a restoration of the stresses which partially relaxed owing to segregation. In the process under discussion, the appearance of concentration nonuniformity is the only mechanism for relaxation of the existing stresses.

Here it should be noted that the idea of segregation resulting from ascending diffusion was qualitatively stated by S. T. Konobeevskiĭ and Ya. P. Selisskiĭ back in 1933.[12] However, S. T. Konobeevskiĭ published the theory of the effect, constructed under the same assumptions as V. S. Gorskiĭ's theory, substantially later in 1943,[13] and he used it to give a qualitative explanation of some experimentally observed properties of binary alloys.

There evidently should exist a maximum segregation-induced dimensionless change in concentration $|\Delta c/c|^*$ as a result of ascending diffusion. This circumstance should be a direct consequence of the fact that the segregation of atoms of a definite type, accompanying ascending diffusion, is accompanied by a lowering of the configurational entropy of a disordered solution, which is obviously disadvantageous.

We shall present an estimate of $|\Delta c/c|^*$ obtained by V. S. Gorskiĭ for a disordered two-component solid substitution solution of substances A and B in a plate with a thickness of $2h$ bent along a radius R. The bending of the plate is a method for creating a field of nonuniform elastic stresses: the maximum tension on the convex surface and maximum compressibility on the concave surface of the plate. Their magnitude is $|\sigma_{max}|$.

The estimate of $|\Delta c/c|^*$ is as follows:

$$\left|\frac{\Delta c}{c}\right|^* = (1-c)\frac{d\varepsilon}{dc}\frac{\tilde{\omega}\,|\sigma_{max}|}{kT}, \tag{4}$$

i.e., the maximum degree of segregational change in the concentration is proportional to $|\sigma_{max}|$. In accordance with the geometry of the sample the estimate of the maximum values of σ_{max} in the elastic region near the stretched and compressed surfaces of the bent plate is as follows: $|\sigma_{max}| = Eh/R$.

Thus

$$\left|\frac{\Delta c}{c}\right|^* = (1-c)\frac{d\varepsilon}{dc}\frac{\tilde{\omega}Eh}{kTR}. \tag{5}$$

For $c\approx 5\cdot 10^{-1}$, $E = 10^{12}$ dynes/cm², $d\varepsilon/dc\approx 10^{-1}$, $h/R\approx 10^{-3}$, $\tilde{\omega}\approx 10^{-23}$ cm³, $kT\approx 10^{-13}$ ergs it turns out that $|\Delta c/c|^*\approx 10^{-2}$.

Equilibrium segregation appears in many real processes. A classical example of such a process is the formation

of impurity clouds around dislocations, in particular, Cottrell clouds. In this case the stress field is determined by the dislocation, and therefore the segregation of the impurity around a stationary dislocation has an equilibrium character.

If the cloud around the dislocation is formed from a supersaturated solution of atoms, then their flow toward the core of the dislocation occurs both under the influence of the chemical part of the gradient of the chemical potential and in the regime of diffusion drift, determined by the tendency for the stress field around the dislocation line and localized around the impurity atom to relax. In many real crystals the segregation cloud around the dislocation, as is well known, decomposes into "drops" decorating this line.[15]

We have discussed above some phenomena which are caused by a common physical factor. We have in mind the diffusion aftereffect in the static state, diffusion aftereffect in the dynamic state (diffusion internal friction), and equilibrium static segregation. Their common cause, foreseen and studied by V. S. Gorskiĭ in his classical work of 1935, consists of the fact that the local gradients of the elastic stresses in crystalline bodies determine the diffusion drift of atoms, which can be directed opposite to the gradient ∇c, i.e., it can acquire the character of an ascending flow. In the international literature this general effect is rightfully called the Gorskiĭ effect.

KINETIC SEGREGATION

In discussing diffusion segregation as being the result of ascending diffusion in the spirit of Gorskiĭ,[1] we assumed that the only cause of the effect is the difference in the volumes of the constituent atoms of the solid substitution solution. In this model of the process the formation of segregation regions owing to diffusion separation of the components of the solution was explained in a natural manner. Over the years it became obvious that the diffusion formation of segregation regions can also occur in solutions whose components have equal atomic volumes, but different partial coefficients of diffusion.

The possibility for such a process does not follow directly from Gorskiĭ's work, but even in this process there occurs a partial separation of the homogeneous solution, which is a consequence of the flow of atoms in a direction opposite to ∇c, i.e., an ascending diffusion flux. In this we can see the justification for a brief exposition of the ideas on which the explanation of the kinetic diffusion segregation effect is based.

It is convenient to explain the essence of the kinetic diffusion segregation on the example of the simplest case of a disordered two-component solid substitution solution, diffusion in which occurs by means of the vacancy mechanism. In this case the flux of atoms of both types (J_A, J_B) and the vacancy flux (J_v) are related by the equation.

$$J_A + J_B + J_v = 0, \tag{6}$$

indicating that the diffusion occurs along vacancies with a constant number of lattice sites.

Whenever a directed vacancy flux J_v is maintained for

any reason in the alloy, the partial atomic fluxes J_A and J_B will be oriented toward it. The directed diffusion vacancy flux is maintained by some effective force (the generalized force of kinetic origin) $F_{gv} = kT\nabla c_v / c_{v0}$, which must create ascending flows and, as a result of this, diffusion segregation of atoms (c_v is the local and c_{v0} is the equilibrium vacancy concentration). Atoms with a high partial diffusion coefficient should be segregated near the vacancy source, and atoms with a low partial diffusion coefficient should be segregated near sinks. For definiteness we set $D_A > D_B$.

As an example of kinetic segregation we call attention to the problem of diffusion deformation of a single crystal of disordered, two-component, solid, substitution solution, diffusion in which occurs by the vacancy mechanism.

As is well known, diffusion creep of a single-component single crystal occurs under conditions when a flux of atoms flows opposite to the directed flux of vacancies.[16,17] In the case of a two-component single crystal (Fig. 6) under conditions when the compressive stress is applied normally to the end faces, near the surfaces of the sample, owing to the ascending diffusion, the end faces must be enriched with atoms of type B and the lateral faces must be enriched with atoms of type A.

It is easy to show that in this very simple case the maximum degree of segregation is determined by the formula

$$\left|\frac{\Delta c}{c}\right|^* \sim (1-c) \frac{D_A\omega_A - D_B\omega_B}{D_A(1-c) + D_Bc} \frac{\sigma}{kT}. \tag{7}$$

We call attention to two limiting situations:

a) $D_A = D_B = D$. In this case $|\Delta c/c|^* \sim (1-c)$ $(\omega_A - \omega_B)\sigma/kT$. We note that this estimate is close to the estimate (4), which also refers to the case when $D_A = D_B = D$. The vacancy subsystem does not participate in the process described by the estimate (4).

b) $D_A = D, D_B = 0$. In this case $|\Delta c/c|^* \sim \tilde{\omega}_A \sigma/kT$. As follows from the structure of the formula (7), this value of $|\Delta c/c|^*$ is the maximum degree of limiting segregation enrichment, since for $D_B = 0$ the numerator in (7) assumes its maximum value while the denominator assumes its minimum value.

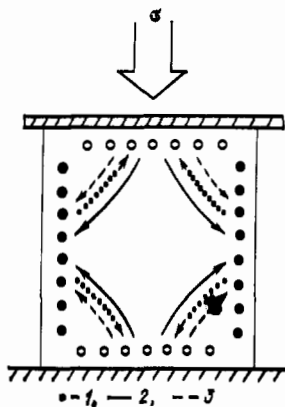An important feature of the segregation effect under

FIG. 6. Diagram of the fluxes accompanying kinetic segregation in a two-component disordered solid solution. 1) Vacancy flux; 2) flux of atoms of type A (●); 3) flux of atoms of type B (○).

discussion[2] is that the limiting degree of segregation in the stationary state of diffusion deformation (creep) remains unchanged because of the fact that the magnitude of the applied stresses, maintaining the constant vacancy flow, remains constant.

In the presence of ascending diffusion, "according to Gorskiĭ," the limiting degree of diffusion segregation is achieved under conditions which do not presuppose the presence of vacancy fluxes and, therefore, the possibility of diffusion transport of mass—diffusion creep in our case.

Kinetic segregation appears in many processes, in particular, in the sintering of powders of alloys. This is convincingly illustrated by an experiment on diffusion sintering of a ball consisting of a two-component alloy and a plate consisting of an alloy with the same composition. The "ball-plane" geometry is the classical geometry in the theory of sintering. It models the initial stage of the process.[19]

As is well known,[19] in the zone of the contact neck, bounded by a surface with negative curvature, there is an active source of vacancies which leave the neck and move into the bulk of the ball and of the plate. The fluxes J_A and J_B, which give rise to expansion of the contact neck, i.e., to sintering, are oriented toward the vacancy flux. Segregation of atoms of the type A should exist in the region of the neck.

The specific peculiarity of the situation under study lies in the fact than an increase in the radius of curvature of the surface, bounding the necks r, accompanying the segregation reduces the vacancy flux, since for the geometry under discussion near the surface of the neck $\Delta c_v / c_{v0} \propto r^{-1}$ and, therefore, $J_v \sim r^{-2}$. This circumstance determines the drop in the dimensionless segregation enrichment of the region of the contact neck by atoms of type A.

The drop in $|\Delta c/c|^*$ during the sintering process in proportion to the growth of the radius of the neck reflects a general feature of the kinetic diffusion segregation: the reduction of J_v is a consequence of the drop in $\Delta c_v / c_{v0}$, and of the force F_{dv}. We note that segregation enrichment can occur in the region near the surface of the contact neck by means of both volume and surface diffusion.

The appearance of segregation regions in the contact zone discussed here was observed clearly[20] in experiments with samples of the solid solutions Cu–In and Cu–Ag. The chemical composition of the samples and their sintering temperature was selected so that the segregation-enriched region near the contact neck would undergo stratification, which facilitates the appearance of a liquid phase differing substantially in chemical composition from the main mass of the sample. The segregation-enriched contact zone was clearly recorded during quenching (Fig. 7).

Diffusion segregation can be illustrated by many different phenomena, where the required directed vacancy flux is

FIG. 7. Diffusion segregation in the alloy Cu + 8 at. % In after sintering ($T = 690$ °C, $t = 16$ h) and subsequent aging ($T = 485$ °C, $t = 12$ h). The arrows mark the regions of segregation (×1500).

maintained either by the curvature of the surface[20,30] or by the difference in the structural state of the constituent parts of the diffusion pair.[21] Amongst all similar effects the effects which have elicited the greatest interest in recent years are the ones which are observed in the presence of radiation action on solids, when in the process of irradiation (with protons, neutrons, ions) a flux of vacancies and interstitial atoms localized by a source of point defects is maintained in the crystal. It is responsible for the segregation of impurities in alloys under irradiation. This effect has been studied in detail in experiments on high-temperature irradiation with protons of silicon containing an impurity, in particular boron atoms. The effect of diffusion segregation is these experiments is manifested as the appearance of a peak in the starting diffusion profile of boron in silicon,[22] or a peak in the boron concentration in the initially uniformly doped silicon crystal.[23] Segregation in alloys accompanying irradiation is discussed in detail in Ref. 24.

[1)]This compound has the following characteristics. In the temperature range above $T = 385$ °C it exists in the cubic form of a disordered stable solid solution. With slow cooling, at $T = 385$ °C, ordering, accompanied by the formation of a face-centered tetragonal lattice, occurs.

[2)]It was predicted in Ref. 18 for polycrystalline objects, where under the conditions of diffusion creep segregation occurs not on free, but rather on intergrain surfaces, which are sources and sinks of vacancies, whose flux is maintained by an externally applied stress.

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