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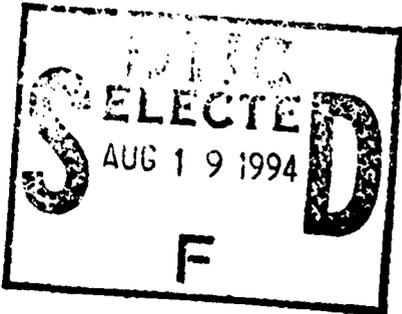
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### ALLOYS AND COMPOSITE MAT'S BR

EVALUATION OF THE FACTORS DETERMINING THE CHANGE IN DIFFUSION  
MOBILITY DURING DEFORMATION

- USSR -

by B. S. Bokshteyn and T. I. Gubkova



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EVALUATION OF THE FACTORS DETERMINING THE CHANGE IN DIFFUSION  
MOBILITY DURING DEFORMATION

- USSR -

[Following is a translation of an article by B. S. Bokshiteyn and T. I. Gubkova in the Russian-language periodical Izvestiya Vysshikh Uchebnykh Zavedeniy, Chernaya Metallurgiya (News of the Higher Educational Institutions, Ferrous Metallurgy) Moscow, No 5, May 1960, pages 108-114.]

It was established earlier [1] that preliminary plastic deformation leads to the acceleration of the diffusion of tin in nickel. This made it possible to suggest that structural changes arising during deformation play a vital role in accelerating the diffusion. As is known, fragmentation of the grains and an increase in the disorientation of adjacent blocks [2] occurs during plastic deformation. Both of these circumstances can lead to the effect under consideration.

On the basis of experimental data obtained in study [1], it is interesting to evaluate quantitatively the role of each of these factors separately: does only the change in the dimensions of the blocks have an influence on the effect observed or in addition to this, is a change in the mobility of the block along the boundaries also significant in the result of deformation?

In this connection, it is necessary to consider the problem of a separate determination of local diffusion characteristics in a real, solid body. First, an attempt to solve such a problem was made by Fischer [3,4]. Later, a more strict solution to the problem of diffusion was presented on the basis of the Fischer model [5, 6].

The model adopted by Fischer has substantial deficiencies as a result of which the size of the grains does not figure directly in the diffusion equations. The Fischer model is not useful for describing diffusion at the boundaries of the mosaic blocks since it describes diffusion in isolated fissures, i.e., it does not take account of the mutual effect of flows from adjacent boundaries to the center of the block or grain.

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Lately another model of the spread of diffusion flows in a real solid body has been proposed [7]. A polycrystal is treated as the wrapping of spheres (of grains, blocks, etc.) of medium size  $r_0$ . The boundaries of the metal grains in this model represent an isolated phase with its customary equilibrium and kinematic characteristics. In a certain average width  $a_0$ , conditions exist in this phase which provide a stepped jump in the concentration and the coefficient of diffusion. The diffusing matter is distributed between two phases: the boundary and the volume of the grain. The model under consideration is close to the model adopted in the theory of thermal transference in granular material [8].

The evaluation of the boundaries of applicability of the model show that with its aid one can describe the progress of the process of diffusion in the volume or along the boundary of the mosaic blocks [7]. These models are satisfied by the following system of equations and boundary conditions:

$$\frac{\partial w}{\partial t} = D_1 \left( \frac{\partial^2 w}{\partial r^2} + \frac{2}{r} \frac{\partial w}{\partial r} \right) \quad (1)$$

$$\frac{\partial u}{\partial t} = D_2 \left( \frac{\partial^2 u}{\partial x^2} - \frac{2}{a_0} D_1 \frac{\partial w}{\partial r} \right) \Big|_{r=r_0} \quad (2)$$

$$u(0, t) = u_0 \quad (3)$$

$$u(x, 0) = 0 \quad (4)$$

$$w(x, r_0, t) = \gamma_0 u(x, t) \quad (5)$$

$$w(x, r) = 0 \quad (6)$$

where  $u$  is the concentration of diffusing matter in the boundary of the block;

$w$  is the concentration of the diffusing matter in the volume of the block;

$D_1$  is the coefficient of diffusion in the volume;

$D_2$  is the coefficient of diffusion along the boundary of the block;

$r_0$  is the average size of the block;

$a_0$  is the width of the boundary;

$t$  is diffusion time;

$x$  is the distance from the surface of the model;

$r$  is the distance from the boundary of the block calculated from its center.

In setting up these equations, the spherical symmetry of the function  $w$  was assumed, which signifies the absence of a gradient of concentration along the boundary at a depth of one block.

The boundary condition (3) satisfies the constancy of the concentration at the boundary of the grain, i.e., the selection of a diffusion problem, and condition (5) takes into account the presence of the equilibrium of the distribution of concentration between the body of the block and its boundary at each moment of time. The distribution occurs in a rather thin layer and is characterized by the constant of dispersion  $\gamma_0$ , which is independent of time.

Let us introduce the dimensionless parameters:

$$\rho = \frac{r}{r_0}; \quad \tau = \frac{D_1 t}{r_0^2}; \quad \xi = \frac{x}{r_0}; \quad \kappa = \frac{D_2}{D_1}$$

Then the equation is rewritten in the following form:

$$\frac{\partial c}{\partial \tau} = \frac{\partial^2 c}{\partial \rho^2}$$

$$\frac{\partial u}{\partial \tau} = \kappa \frac{\partial^2 u}{\partial \xi^2} - \frac{2}{a_0} \frac{\partial}{\partial \xi} \int_0^1 c \rho d\rho \quad (7)$$

where  $c = rw$ .

The boundary conditions:

$$u(\xi, 0) = 0 \quad (8)$$

$$u(0, \tau) = u_0 \quad (9)$$

$$c \Big|_{\rho=1} = \gamma_0 r_0 u = \gamma u^* \quad (\text{For simplification, it will be assumed henceforth that } \gamma_0 = 1) \quad (10)$$

$$c \Big|_{\rho=0} = 0 \quad (11)$$

$$c(\xi, \rho, 0) = 0 \quad (12)$$

The system is solved by the operational method of LaPlace. The exact solution in representation (7) has the form:

$$\frac{\bar{u}}{u_0} = \frac{1}{p} e^{-\sqrt{p + \gamma \frac{2}{a_0}} K(p)} \quad (13)$$

where

$$K(p) = \sqrt{p} \frac{e^{\sqrt{p}} + e^{-\sqrt{p}}}{e^{\sqrt{p}} - e^{-\sqrt{p}}} - 1 = \sqrt{p} \operatorname{cth} \sqrt{p} - 1 \quad (14)$$

and

$$\bar{c} = \gamma \bar{u} \frac{e^{\sqrt{p} a_0} - e^{-\sqrt{p} a_0}}{e^{\sqrt{p}} - e^{-\sqrt{p}}} \quad (15)$$

or

$$\frac{\bar{c}}{\bar{u}_0} = \frac{\gamma}{p} \cdot \frac{e^{\sqrt{p} a_0} - e^{-\sqrt{p} a_0}}{e^{\sqrt{p}} - e^{-\sqrt{p}}} \exp \left( - \sqrt{\frac{p + \gamma \frac{2}{a_0} K(p)}{2}} \right) \quad (16)$$

The solution obtained (13, 16) in the representations exactly satisfy system (1, 2). However, it is cumbersome and precludes the possibility of going from the general form to the original. Further simplifications are connected with the concrete peculiarities of the problem to be solved. Up to the present time the solution has had a quite general character, excluding the assumption of the spherical symmetry of  $w$ .

In this connection, we shall consider in greater detail the question of the limits of applicability of the proposed model.

The absence of a gradient of concentration along the boundary at distances on the order of the size of the block signifies that at any point the following condition should be fulfilled

$$\frac{\partial u}{\partial x} r_0 \ll 1. \quad (17)$$

or

$$r_0 \ll \frac{D_2}{D_1} \frac{a_0}{\gamma_0 K(p)} \quad (18)$$

The evaluation shows that in considering the process of diffusion along the blocks and between them, condition (18) is always satisfied.

We shall assume that in the period of diffusion annealing, the diffusing matter penetrates to a distance exceeding 100 times the size of the block. These conditions are fulfilled in the experiments. Then  $\gamma = \frac{t}{r_0^2} \gg 1$  and inasmuch as  $\frac{1}{\tau} \ll p$

$$\frac{1}{D_1}$$

(consequently  $p \ll 1$ ), but

$$\lim_{p \rightarrow 0} K(p) = \frac{1}{3} p$$

one can compute with a high degree of precision

$$K(p) \approx \frac{1}{3} p.$$

In addition, assuming that  $1 \ll \frac{2}{3} \frac{\gamma}{a_0}$ , in place of (13) we obtain

$$\frac{u}{u_0} \approx \frac{1}{p} e^{-\beta \sqrt{p}} \quad (19)$$

where

$$\beta = \sqrt{\frac{2}{3} \frac{\gamma}{a_0}} \quad (20)$$

Let us make the transition to the original

$$\frac{1}{p} e^{-\beta \sqrt{p}} + \operatorname{erfc} \frac{\beta}{2 \sqrt{\tau}}$$

where  $\operatorname{erfc}(x) = 1 - \operatorname{erf}(x)$ .

Consequently,

$$\frac{u}{u_0} = \operatorname{erfc} \frac{\beta}{2 \sqrt{\tau}} \quad (21)$$

Making the transition now to function  $w$ , we obtain from (15)

$$\bar{w} = \bar{u} \frac{e^{-\sqrt{p}x} - e^{-\sqrt{p}l}}{e^{-\sqrt{p}x} - e^{-\sqrt{p}l}} \quad (22)$$

Since  $\sqrt{p}l \ll 1$ , we have

$$\frac{e^{-\sqrt{p}x} - e^{-\sqrt{p}l}}{e^{-\sqrt{p}x} - e^{-\sqrt{p}l}} \approx \frac{2 - \sqrt{p}l}{2 - \sqrt{p}l} \quad (23)$$

The equality  $\bar{w} = \bar{u}$  follows from (22) and (23) which leads to the relationship

$$\frac{w}{u_0} = \frac{u}{u_0} = \operatorname{erfc} \frac{\beta}{2\sqrt{t}} \quad (24)$$

The absence of the dependence of  $w$  on  $r$  and also the equality of the concentration of diffused matter in the block and at the boundary of the block are a natural consequence of the requirement concerning the penetration of diffused matter to a depth which significantly exceeds the dimensions of the block.

Inasmuch as it is not possible to observe directly the flow along the boundaries and in the block using the method of autoradiography, we find the average concentration of diffused matter in the grain ( $w_{\text{average}}$ ) depending on the depth of penetration and the time period, taking account of the portion of the surface occupied by the boundaries and the body of the blocks.

$$w_{\text{cp}} = \frac{u_2 \pi r_0 a_0 + w \pi r_0^2}{2 \pi r_0 a_0 + \pi r_0^2}$$

Or, since  $a_0 \ll r_0$

$$w_{\text{ave}} \approx w. \quad (25)$$

From (25) and (24), it follows:

$$\frac{w_{cp}}{u_0} = \operatorname{erfc} \frac{\beta}{2\sqrt{\tau}} \quad (26)$$

Let us estimate the order of magnitude of

$$\frac{\beta}{\sqrt{\tau}}$$

In accordance with (20)

$$\beta \approx \frac{\beta}{\sqrt{x}} \sqrt{\frac{r_0}{a_0}}$$

The analysis of experimental data makes it possible to give the following values to the elements of this expression:

$$x \sim 10^2 \text{ -- } 10^3; \quad \frac{r_0}{a_0} \sim 10^3 \text{ -- } 10^4$$

and  $\beta \sim 10^2$

in accordance with the suggestion on the processing of a large number of blocks. When it follows  $\tau \sim 10^2$  and  $\sqrt{\tau} \sim 10$ .

Thus  $\beta > 10^2$  and  $\frac{\beta}{\sqrt{\tau}} > 10$  and this means that one can use an asymptotic expansion

$$\operatorname{erfc} \frac{\beta}{2\sqrt{\tau}} \approx \frac{2}{\beta} \sqrt{\frac{\tau}{\pi}} e^{-\frac{\beta^2}{4\tau}} \quad (27)$$

From (26) and (27), it follows:

$$\frac{w_{cp}}{u_0} = \frac{A}{x} e^{-cx^2} \quad (28)$$

where

$$A = \sqrt{\frac{6}{\pi}} \sqrt{\frac{D_2 a_0 t}{r_0}} \quad (29)$$

$$C = \frac{r_0}{6a_0 D_2 t} \quad (30)$$

Let us introduce logarithms in (28):

$$\ln w_{cp} = \ln(u_0 A) - \ln x - Cx^2 \quad (31)$$

It is clear that if  $\ln x \ll Cx^2$ , then the second element in equation (31) can be ignored (in comparison with the value of the third element) and  $\ln w_{ave}$  can be considered proportion to  $x^2$ . The evaluation shows that this condition is always satisfied when  $x \sim 10^{-3}$  cm. For lesser values of the depth of penetration one actually observes a deviation in the dependence  $\ln w_{ave} - x^2$  from the linear.

It is easy to see that

$$\frac{D_2}{r_0} = \frac{1}{6a_0 t C} \quad (32)$$

Thus, processing the experiments obtained can lead to a determination of the ratio  $\frac{D_2}{r_0}$  and its change under the influence

of deformation. However, the analysis of one of this quantity does not provide an answer to the problem posed since its increase can be caused by increasing  $D_2$  as well as by decreasing  $r_0$ .

In order to determine the relative role of the change in these two parameters, it is necessary to enlist some values. It is expedient to take into consideration the effective coefficient of diffusion in the grain  $D_3$ , obtained earlier in processing experiment [1] mentioned above. Since the coefficient of diffusion along the boundaries of the blocks significantly exceeds the coefficient of diffusion within the blocks, one may expect the crushing of the block to increase the effective coefficient of diffusion in the grain in proportion to the surface of the blocks.

Actually, for large values of  $D_2$ , the speed of diffusion within the grain must be determined by  $D_1$  and the surface of the blocks and will not grow noticeably with an increase in  $D_2$ . Thus, one may expect  $D_3$  to be proportional to  $\frac{1}{r_0}$ . Comparing the change

in  $\frac{D_2}{r_0}$  with the change in  $D_3$ , one can establish separately the role of the factors under consideration.

The results of such calculations for the case of the diffusion of tin in nickel are presented in Tables 1 and 2 (for the calculations, it was assumed  $a_0 = 5 \cdot 10^{-8}$  cm).

An analysis of the experimental data shows that the increase in the effective coefficient of diffusion in the grain, observed as a result of deformation, is explained by the fragmentation of the grains and the decrease in the sizes of the blocks of mosaics. Actually, the constancy of the ratio  $\frac{D_3}{\frac{D_2}{r_0}}$  (last column in Tables

1 and 2) indicates that  $D_3$  increases in proportion to the surface of the blocks ( $\frac{1}{r_0}$ ), and  $D_2$  practically does not change with an

increase in the degree of deformation. (In this regard, the unlikely hypothesis that  $D_2$  changes as  $D_1$  is not considered.)

TABLE 1

RESULTS OF CALCULATIONS FOR THE DIFFUSION OF TIN IN NICKEL,  
WHICH HAS UNDERGONE PRELIMINARY COLD DEFORMATION WITH SUBSEQUENT  
ANNEALING FOR 125 HOURS

Annealing Temperature, °C.	Degree of Deformation $\epsilon$ , %	C	$\frac{D_2}{r_0}$ , cm/sec	$D_3$ , cm <sup>2</sup> /sec	$\frac{D_3}{D_2}$ , cm $r_0$
700	-	$80 \cdot 10^5$	$0.09 \cdot 10^{-5}$	$0.7 \cdot 10^{-13}$	$7.8 \cdot 10^{-8}$
	10	$50 \cdot 10^5$	$0.15 \cdot 10^{-5}$	$8.4 \cdot 10^{-13}$	$56 \cdot 10^{-8}$
	60	$4 \cdot 10^5$	$1.83 \cdot 10^{-5}$	$14 \cdot 10^{-13}$	$7.7 \cdot 10^{-8}$
800	-	$10.8 \cdot 10^5$	$0.68 \cdot 10^{-5}$	$5.2 \cdot 10^{-13}$	$7.7 \cdot 10^{-8}$
	5	$2.5 \cdot 10^5$	$2.93 \cdot 10^{-5}$	$23 \cdot 10^{-13}$	$7.5 \cdot 10^{-8}$
	10	$1.2 \cdot 10^5$	$6.10 \cdot 10^{-5}$	$46 \cdot 10^{-13}$	$7.6 \cdot 10^{-8}$

TABLE 2

RESULTS OF CALCULATIONS FOR THE DIFFUSION OF TIN IN NICKEL,  
WHICH HAS UNDERGONE PRELIMINARY COLD DEFORMATION WITH SUBSEQUENT  
ANNEALING FOR 100 HOURS

Annealing Temperature, °C.	Load, ε, kg/mm <sup>2</sup>	Degree of Deformation , %	$0 \cdot 10^{-5}$	$\frac{D_2}{r_0^2 \cdot 10^5}$ cm/sec $\cdot 10^5$	$\frac{D_3 \text{ cm}^2}{\text{sec} \cdot 10^{13}}$	$\frac{D_3}{D_2} \cdot 10^3$ cm $\cdot 10^3$
750	-	-	2.4	3.8	27	7.1
	1.5	-	0.75	12.2	70	5.7
	3.0	4.6	0.57	16.1	87	5.4
	3.5	16.2	0.31	29.6	180	6.1
	4.0	20.0	0.25	36.6	230	6.3
4.5	25.2	0.19	48.2	390	8.1	
850	-	-	0.34	27.0	210	7.0
	0.3	-	0.19	48.2	410	8.5
	1.5	10.2	0.15	61.1	640	10.4
	2.0	15.0	0.086	106.5	800	7.5
	2.5	18.5	0.07	130.8	1000	7.7
900	-	-	0.14	65.5	500	7.6
	0.3	-	0.08	114.5	870	7.6
	0.5	2.0	0.07	130.8	1000	7.7
	1.0	9.6	0.063	145.5	1120	7.7
	1.5	16.8	0.054	169.7	1300	7.7
2.0	22.0	0.05	183.2	1400	7.5	

If  $r_0$  is assumed to be on the order of  $10^{-5}$  cm. it follows from the data presented in conjunction with the hypothesis mentioned that  $\frac{D_2}{D_3} = 10^2$ .

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