Acceleration of grain boundary motion in Al by small additions of Ga

By D. A. MOLODOV†, U. CZUBAYKO†, G. GOTTSTEIN†,
L. S. SHVINDLERMAN‡, B. STRAUMAL‡§ and W. GUST§

† Institut für Metallkunde und Metallphysik, Rheinisch-Westfälische Technische Hochschule Aachen, D-52056 Aachen, Germany
‡ Institute of Solid State Physics, Russian Academy of Science, Chernogolovka, Moscow District 142432, Russia
§ Institut für Metallkunde der Universität and Max-Planck-Institut für Metallforschung, Seestrasse 75, D-70174 Stuttgart, Germany

ABSTRACT

The temperature dependence of $\langle 111 \rangle$ tilt grain boundaries with angles of misorientation of $38 \cdot 2°$ and $40 \cdot 5°$ was investigated in bicrystals of both pure (99·999%) Al and the same Al doped with 10 ppm Ga in the temperature regime between 400 and 580°C. The grain boundary mobility for the investigated grain boundaries over the entire investigated temperature range is enhanced by minor additions of Ga. Both the activation enthalpy and the pre-exponential factor are affected by Ga doping. The orientation dependence of grain boundary mobility is strongly reduced but not completely removed. The drastic rise in grain boundary mobility by the addition of Ga to pure Al is interpreted as a consequence of a change in the boundary structure and the mechanism of boundary migration owing to a pre-wetting phase transition and formation of a liquid (or quasiliquid) Ga-rich layer on the grain boundary.

§ 1. INTRODUCTION

There is unambiguous evidence that grain boundary motion in metals is influenced by impurities. This is accounted for by the impurity drag theories (Lücke and Detert 1957, Cahn 1962, Lücke and Stüwe 1963), which predict a decrease in the effective grain boundary mobility by impurity drag. All known experiments on bicrystals and polycrystals confirm that solute atoms reduce the boundary migration rate. Several experiments have demonstrated that the extent of impurity drag depends on impurity type and grain boundary structure. Therefore the total impurity content is not an adequate parameter to characterize the solute–boundary interaction and its effect on boundary motion. Instead it is required to investigate the effect of solutes on grain boundary motion in high purity material doped with small quantities of specific impurities. Owing to a non-zero background impurity level even in the purest material, the content of the impurity under investigation has to exceed the concentration of other solutes in this material.

The subject of the current investigation was the measurement of grain boundary mobility in bicrystals of pure Al with minor Ga additions. The element Ga is known to generate conspicuous effects in Al. In higher concentrations it leads to intergranular embrittlement which can be used to decompose Al polycrystals. Also it influences strongly the transition from normal to abnormal grain growth in Al (Sursaeva *et al.* 1995). Moreover, Ga was found to speed up discontinuous precipitation in supersaturated Al-Ag alloys (Predel and Gust 1972). Since discontinuous precipitation occurs

at moving grain boundaries, Ga may also affect the mobility of grain boundaries in pure Al. The current investigation was designed to investigate systematically the influence of Ga on the process of grain-boundary migration in Al.

§2. GRAIN BOUNDARY GEOMETRY AND EXPERIMENTAL PROCEDURE

The mobility of individual $\langle 111 \rangle$ tilt grain boundaries with misorientations of $38 \cdot 2^\circ$ (special boundary with $\Sigma = 7$) and $40 \cdot 5^\circ$ was studied. These types of boundary were chosen, since it is known from other experiments (Gottstein, Molodov, Czubayko and Shvindlerman 1995, Molodov, Czubayko, Gottstein and Shvindlerman 1995) that these boundaries exhibit the highest mobility in pure Al, although in different but complementary temperature ranges (Molodov *et al.* 1995). Correspondingly, these two boundaries effectively control the recrystallization texture development in Al and therefore are of prime interest for recrystallization processing.

The experiments were carried out on bicrystals of both very pure (99·999%) Al and the same Al doped with 10 ppm Ga. The driving force for grain boundary motion was provided by the boundary curvature, which remained constant for the bicrystal geometry used (fig. 1). To study the characteristics of migration, successive high-temperature anneals were carried out and the change in grain boundary position with time was recorded. For *in-situ* measurements of grain boundary motion a specially designed X-ray continuous tracking device was used. Details of sample preparation, measuring procedure, device and accuracy have been given elsewhere (Molodov *et al.* 1994, 1995, Czubayko, Molodov, Petersen, Gottstein and Shvindlerman 1995, Gottstein *et al.* 1995).

§3. RESULTS

The velocity v of a moving grain boundary under a driving force p is given by

$$v = mp, \tag{1}$$

where m is the grain boundary mobility. In the current experiments the driving force remained constant, namely $p = \sigma/a$, where σ is the grain boundary surface tension and

Fig. 1.
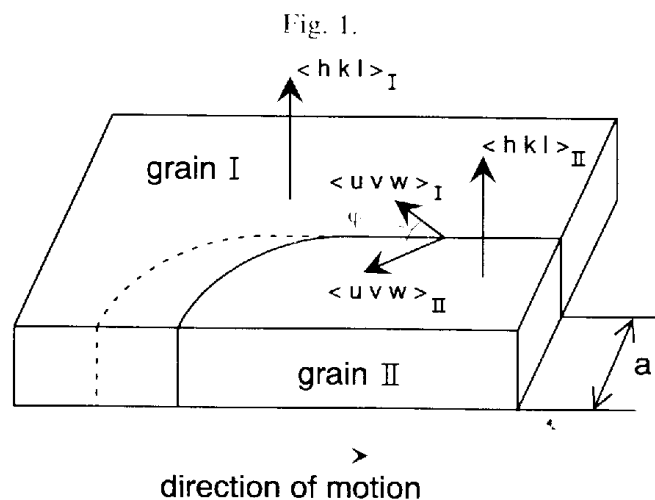
Bicrystal geometry for grain-boundary motion measurements under a constant driving force: (⟶), current; (- - -), prior grain-boundary location.

a is the width of the shrinking grain. The quantity of interest is the mobility m. For convenience we use the reduced mobility

$$A \equiv va = m\sigma = A_0 \exp\left(-\frac{H}{kT}\right),$$ (2)

where H is the activation enthalpy of boundary mobility and A_0 algorithm the pre-exponential mobility factor. As evident from fig. 2, in the investigated temperature range the grain boundary mobility is found to be much higher in Al + 10 ppm Ga than in pure Al for both 38·2° and 40·5°, $\langle 111 \rangle$ tilt boundaries. The activation enthalpy for the 38·2° $\langle 111 \rangle$ tilt boundary was found to be slightly higher in Ga-doped Al than that in pure Al. In contrast, the 40·5°, $\langle 111 \rangle$ tilt boundary exhibits a distinctly lower activation enthalpy in Al + 10 ppm Ga than in pure Al (table). The absolute difference of the activation enthalpies of both investigated boundaries decreases upon Ga addition (fig. 3).

§4. DISCUSSION

In effect there are three major results that deserve special attention.

(1) For all investigated grain boundaries the mobility is improved rather than degraded by minor additions of Ga.
(2) Both the activation enthalpy H and the pre-exponential factor A_0 are affected by Ga doping. For the $\Sigma = 7$ boundary, H and A_0 increase, but H and A_0 decrease for the 40·5°, $\langle 111 \rangle$ boundary.
(3) The orientation dependence of grain boundary mobility is strongly reduced but not entirely removed. Although the values of H and A_0 for the different boundaries in the Ga-doped material are much closer than in pure Al, the values remain distinctly different even when accounting for the measuring inaccuracy.

The influence of impurities on grain boundary motion has been frequently investigated both theoretically (Lücke and Detert 1957, Cahn 1962, Lüche and Stüwe 1963, Hillert and Sundman 1976, Westengen and Ryum 1978, Aristov, Fradkov and Shvindlerman 1980, Molodov, Fradkov, Shvindlerman and Kaplan 1984) and experimentally (Aust and Rutter 1959, Fridman, Kopezki and Shvindlerman 1975, Dimitrov, Fromageau and Dimitrov 1978, Gottstein and Shvindlerman 1992) in the past. In the well known approach of Lücke and Detert (1957), Lüche and Stüwe (1963) and Cahn (1962), a boundary is considered to attract impurity atoms, which reduce the driving force p to an effective driving force $p_{\rm eff}$:

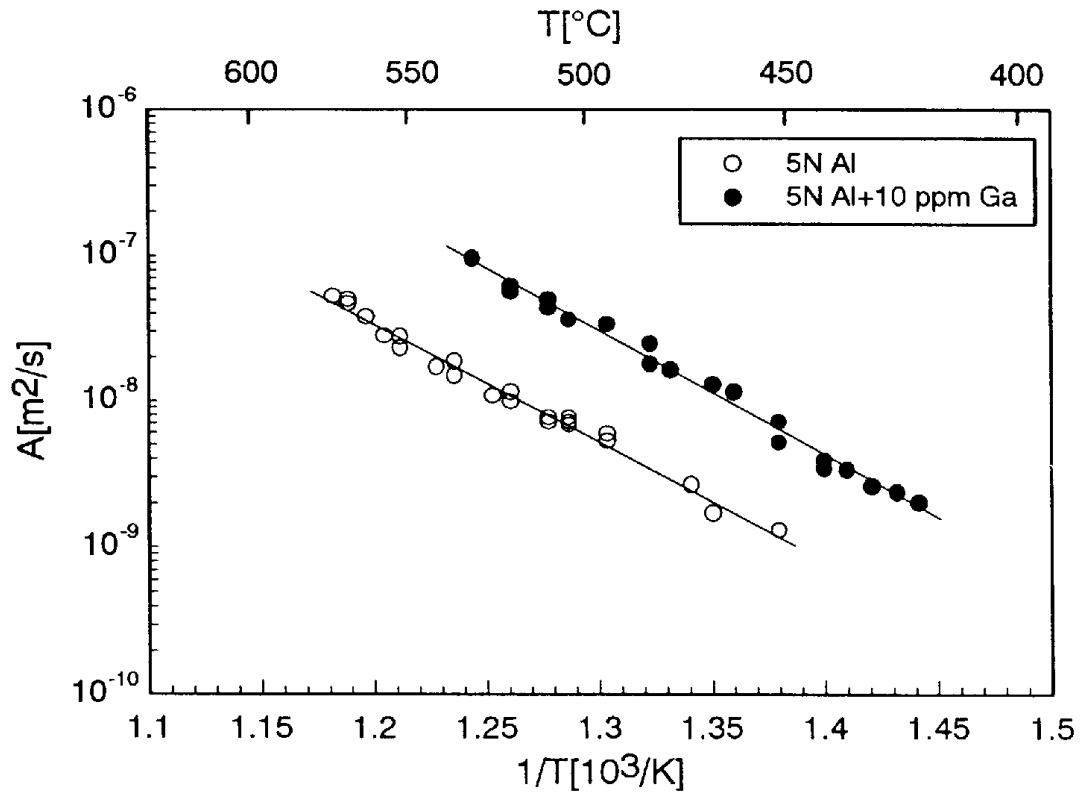$$p_{\rm eff} = p - \Gamma f,$$ (3)

where Γ is the concentration of adsorbed impurity atoms and f the interaction force between individual impurities and the grain boundary. According to eqn. (1) the grain boundary migration rate reads

$$v = m p_{\rm eff}.$$ (4)

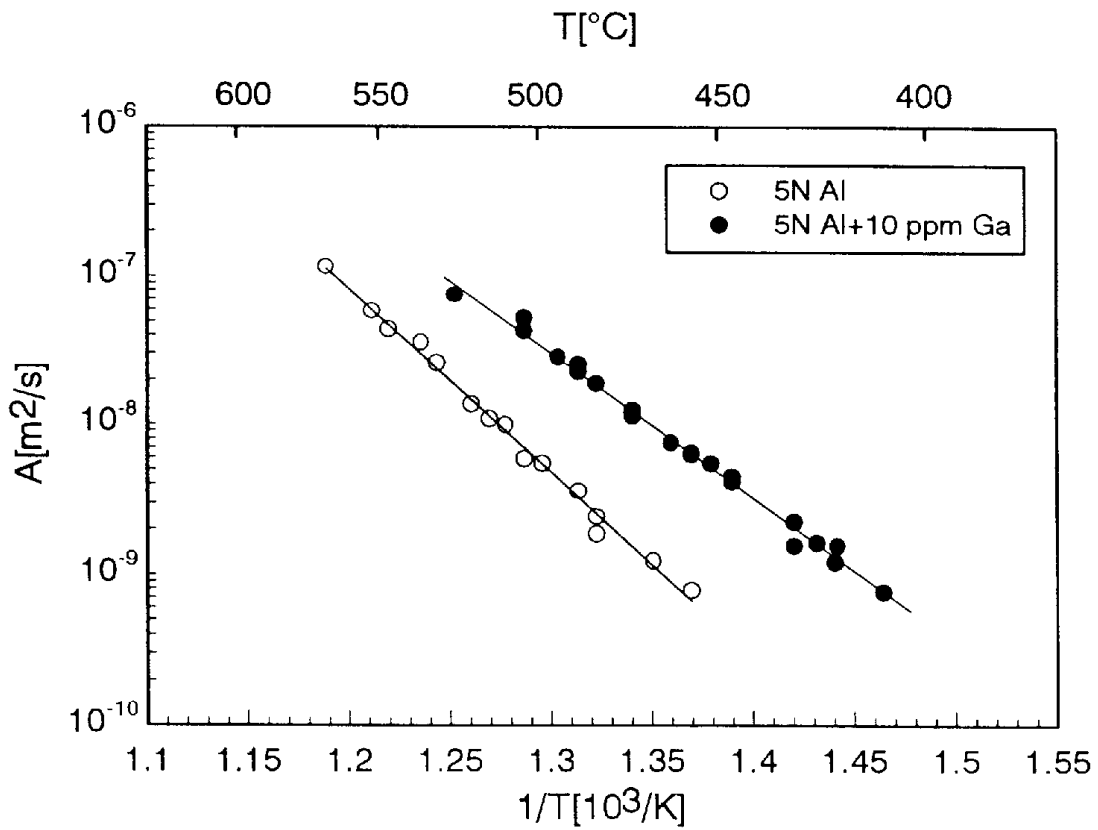For the joint motion of the boundary with absorbed impurity atoms impurity, drag theory predicts

$$v = \frac{mp}{1 + \Gamma(kT/D)m},$$ (5)

Fig. 2.

(a)

(b)

Arrhenius plot of mobility of (a) 38·2° and (b) 40·5°, ⟨111⟩ tilt grain boundaries in pure Al and pure Al doped with 10 ppm Ga.

Migration parameters of investigated $\langle 111 \rangle$ tilt grain boundaries.

Material	Tilt angle (degrees)	Activation enthalpy (eV)	Pre-exponential factor $(m^2 s^{-1})$
Al(99·999%)	38·2 ± 0·4	1·61 ± 0·08	$1·5 \times 10^2 \pm 7·5$
Al(99·999%)	40·5 ± 0·4	2·46 ± 0·12	$4·9 \times 10^7 \pm 2·5 \times 10^6$
Al + 10^{-3}% Ga	38·2 ± 0·4	1·72 ± 0·09	$4·7 \times 10^3 \pm 2·4 \times 10^2$
Al + 10^{-3}% Ga	40·5 ± 0·4	1·94 ± 0·10	$1·4 \times 10^5 \pm 7·0 \times 10^3$

where D is the volume diffusion coefficient of the impurities. It is evident from eqn. (5) that impurities always slow down grain-boundary motion.

This fundamental theoretical approach was frequently modified and improved by other workers, taking into account details of the migration and interaction process, but invariably the result is a deceleration of the moving boundary by impurity atoms. This is at variance, however, with the result of the current investigation, which substantiates an acceleration of grain boundary motion by Ga in Al. Evidently, the obtained experimental results cannot be interpreted in terms of an interaction between individual impurity atoms and a moving grain boundary, since this interaction (no matter whether attractive or repulsive) will always result in a reduction in grain boundary mobility.

Fig. 3.
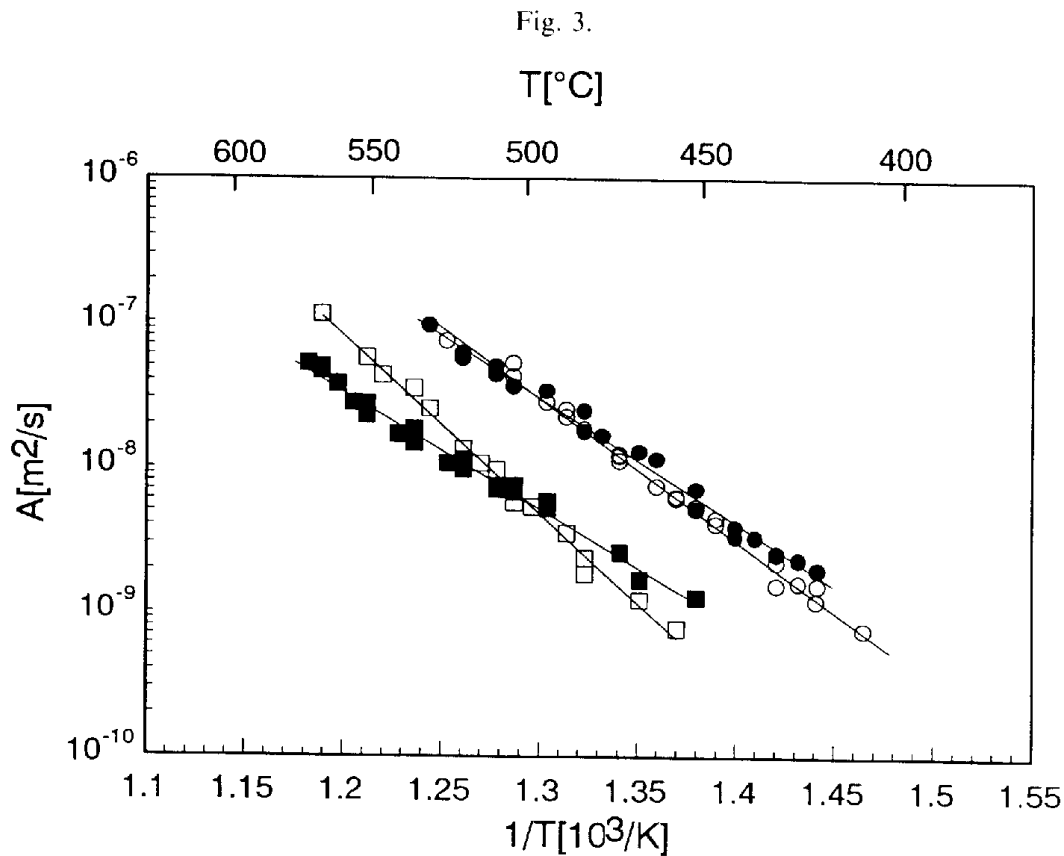
Temperature dependence of mobility of 38·2° (●, ■) and 40·5° (○, □) $\langle 111 \rangle$ tilt grain boundaries in Al (□, ■) and Al + 10 ppm Ga (○, ●).

The change in activation enthalpy H as well as the pre-exponential factor A_0 upon Ga addition indicates that there might be a change in the mechanism of grain boundary motion owing to a change in grain boundary structure. This is particularly apparent from the fact that H and A_0 change differently for the two investigated boundaries; for the 38·2° ($\Sigma = 7$) boundary, H and A_0 increase, while they decrease for the 40·5° boundary, although they do not become uniform for all boundaries. Since Ga is known to segregate to grain boundaries and to cause intergranular embrittlement at larger concentrations, we propose to attribute the effect of Ga on grain boundary mobility to the formation of a layer of a second phase on the grain boundary in Ga-doped Al, for instance by a grain boundary pre-wetting phase transition and correspondingly by the formation of a liquid (or quasiliquid) film of Ga on the grain boundary (Rabkin, Shvindlerman and Straumal 1991).

From thermodynamic considerations (Clark 1987) the equilibrium thickness δ_0 of an interfacial layer of a second phase, which is stable on the grain boundary but not stable in the bulk, is given by

$$\delta_0 = \xi \ln\left(\frac{4\Phi_0}{\Delta g}\right), \tag{6}$$

where ξ is the correlation length, Φ_0 is the energy parameter related to the specific heat of melting and Δg is the excess free-energy density of the wetting phase. Since no data on ξ, Φ_0 and Δg are available, there is no way to predict the thickness of the grain boundary wetting phase. Because of the known strong segregation behaviour of Ga to grain boundaries and the failure of models based on interactions between boundary and individual impurity atoms, we shall consider the hypothesis that a continuous Ga-rich layer will form in the boundary upon Ga addition. No doubt, the structure of a grain boundary will become substantially altered by the occurrence of a wetting phase interlayer. The usually observed or computed narrow grain boundary structure must change to a relatively wide interlayer structure, actually with two interphase boundaries, namely one on each side of the interlayer. Correspondingly, the mechanism of grain boundary motion is bound to change, in its simplest form from a short-range transfer to a multiple detachment–attachment jump sequence as proposed by Gleiter (1969) or Haessner and Hofmann (1971) in the past. The grain boundary mobility is determined by the slowest process in the sequence of atomic transfer across the boundary. If the interlayer is a wetting phase, the activation energy for mass transport across it ought to correspond roughly to the activation energy for diffusion in liquids, which is of the order of 0·1 eV, that is much smaller than the measured energy of activation for grain boundary motion and therefore at variance with the experimental results. Consequently, grain boundary mobility must be controlled by the detachment and attachment processes at interlayer–crystal interfaces, irrespective of the thickness of the interlayer as long as the wetting phase is continuous. One might expect that the formation of a liquid interlayer breaks up the equilibrium structure of the single phase boundary and therefore levels the orientation dependence of grain boundary mobility. The activation enthalpy and even the pre-exponential factor of the mobility of both boundaries of the doped material are much closer than in the undoped material, since the activation enthalpy of the 40·5°, $\langle 111 \rangle$ boundary is substantially reduced from 2·2 to 1·9 eV while, for the 38·2° ($\Sigma = 7$) boundary, H rises from 1·5 to 1·8 eV. The pre-exponential factors change accordingly and attain the same order of magnitude for both boundaries. Nevertheless, an

orientation dependence remains, although much less pronounced. This can only be attributed to a misorientation-dependent structure of the grain interlayer interface.

While it seems acceptable that the activation enthalpy for grain boundary motion decreases upon formation of an interlayer (as found for the 40·5°, ⟨111⟩ boundary), it is not obvious why the corresponding activation enthalpy of the $\Sigma = 7$ boundary would increase. In this context, one has to recognize that not only the activation enthalpy but also the pre-exponential factor increased to compensate for the rise of the activation enthalpy such that the absolute value of mobility increased. There are two obvious reasons for the rise of H (38·2° ($\Sigma = 7$) boundary), namely impurity drag due to the interlayer atoms or more difficult transfer of atoms through the crystal interlayer interface. The decrease in H (40·5° boundary) upon Ga addition indicates that the Ga atoms of the interface layer do not exert a strong drag on the boundary, most probably because of the high mobility of Ga atoms in the boundary. The similarity of activation parameters for both boundaries in the Ga-doped Al hints at the importance of the transfer mechanism of Al atoms through the Al Ga interface. However, the small but distinct difference between H ($\Sigma = 7$) and H (40·5°, ⟨111⟩) substantiates that, even though the transport phenomena at the Al surfaces on both sides of the Ga interlayer play a dominant role for the migration process, they remain orientation dependent, that is the crystal–interlayer interface structure depends on misorientation across the boundary.

In summary, the formation of a wetting Ga-rich phase on the grain boundary drastically changes the grain boundary structure and the mechanisms of grain boundary migration. Instead of short-range atomic transfer processes and impurity drag, grain boundary motion is controlled by mass transfer across a wide grain boundary, where the detachment–attachment processes at the crystal interlayer interfaces become dominant. Correspondingly, irrespective of the structure and segregation behaviour of the corresponding boundaries in the pure material, minor additions of Ga drastically affect grain boundary structure and enhance grain boundary mobility.

REFERENCES

ARISTOV, V. YU., FRADKOV, V. E., and SHVINDLERMAN, L. S., 1980, *Soviet Phys. solid St.*, 22, 1055.
AUST, K. T., and RUTTER, J. W., 1959, *Trans. AIME*, 215, 119, 820.
CAHN, J. W., 1962, *Acta metall.*, 10, 789.
CLARKE, D. R., 1987, *J. Am. Ceram. Soc.*, 70, 15.
CZUBAYKO, U., MOLODOV, D. A., PETERSEN, B.-C., GOTTSTEIN, G., and SHVINDLERMAN, L. S., 1995, *Measure Sci. Technol.*, 6, 947.
DIMITROV, O., FROMAGEAU, R., and DIMITROV, C., 1978, *Recrystallization of Metallic Materials*, edited by F. Haessner (Stuttgart: Riederer), p. 137.
FRIDMAN, E. M., KOPEZKI, CH. V., and SHVINDLERMAN, L. S., 1975, *Z. Metallk.*, 66, 533.
GLEITER, H., 1969, *Acta metall.*, 17, 853.

GOTTSTEIN, G., and SHVINDLERMAN, L. S., 1992, *Scripta metall. mater.*, **27**, 1515.
GOTTSTEIN, G., MOLODOV, D. A., CZUBAYKO, U., and SHVINDLERMAN, L. S., 1995, *J. Phys. IV C3*, **5**, 89.
HAESSNER, F., and HOFMANN, S., 1971, *Z. Metallk.*, **62**, 807.
HILLERT, M., and SUNDMAN, B., 1976, *Acta metall.*, **24**, 731.
LÜCKE, K., and DETERT, K., 1957, *Acta metall.*, **5**, 628.
LÜCKE, K., and STÜWE, H., 1963, *Recovery and Recrystallization of Metals*, edited by L. Himmel (New York: Interscience), p. 171.
MOLODOV, D. A., CZUBAYKO, U., GOTTSTEIN, G., and SHVINDLERMAN, L. S., 1995, *Scripta metall. mater.*, **32**, 529.
MOLODOV, D. A., SWIDERSKI, J., GOTTSTEIN, G., LOJKOWSKI, W., and SHVINDLERMAN, L. S., 1994, *Acta metall. mater.*, **42**, 3397.
MOLODOV, D. A., FRADKOV, V. E., SHVINDLERMAN, L. S., and KAPLAN, G. I., 1984, *Soviet Phys. solid St.*, **26**, 284.
PREDEL, B., and GUST, W., 1972, *Mater. Sci. Engng*, **10**, 239.
RABKIN, E. I., SHVINDLERMAN, L. S., and STRAUMAL, B. B., 1991, *Int. J. mod. Phys.* B, **5**, 2989.
SURSAEVA, V., STRAUMAL, B., RISSER, S., CHENAL, B., GUST, W., and SHVINDLERMAN, L., 1995, *Phys. Stat. sol.* (a), **149**, 379.
WESTENGEN, H., and RYUM, N., 1978, *Phil. Mag.* A, **38**, 279.