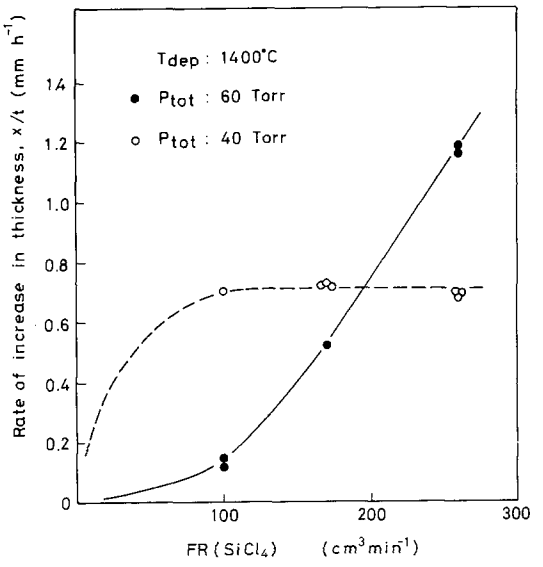

Figure 1 Effect of the $SiCl_4$ (vapour) flow rate on the rate of increase in thickness of Py–Si_3N_4.

$(NH_3)]$, 60 $cm^3\ min^{-1}$; $SiCl_4$(v) to H_2 gas flow rate ratio $FR(SiCl_4)/FR(H_2)$, ~0.26; $SiCl_4$(v) flow rate $[FR(SiCl_4)]$, 100, 170 and 260 $cm^3\ min^{-1}$.

Fig. 1 shows the relationship between x/t and $FR(SiCl_4)$. At $P_{tot} = 40$ Torr, x/t ranges from 0.68 to 0.73 mm h^{-1}, while at $P_{tot} = 60$ Torr it increases with increasing $FR(SiCl_4)$ and reaches 1.2 mm h^{-1} at $FR(SiCl_4) = 260\ cm^3\ min^{-1}$. Above $FR(SiCl_4) = 260\ cm^3\ min^{-1}$, the deposited layer on the substrate is heterogeneous at $P_{tot} = 60$ Torr.

Structural characteristics of Py–Si_3N_4 formed at $x/t = 1.2$ mm h^{-1} are as follows: the crystal structure is α-type; the lattice parameters are $a = 7.752 \pm 0.002$ Å and $c = 5.622 \pm 0.002$ Å; the density is 3.18 g cm^{-3} (100% of a theoretical density); and the (2 2 2) plane is parallel to the deposition surface.

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TOSHIO HIRAI
KOICHI NIIHARA
TAKASHI GOTO
The Research Institute
for Iron, Steel and Other Metals,
Tohoku University,
Sendai, 980, Japan

Non-unique stress–strain-rate relations during superplastic flow

Isothermal superplastic deformation of a material of constant grain size is usually represented by an equation of the type [1–3]

$$\sigma = k\dot{\epsilon}^m \qquad (1)$$

where σ is the applied stress, $\dot{\epsilon}$ the strain-rate, m the strain-rate sensitivity index, and k an empirical constant. This equation implies that the magnitude of stress corresponding to a given strain-rate is independent of the *path* by which that strain-rate is reached. Further, it has been reported that strain-rate compensated true stress–true strain curves exhibit practically no work-hardening when the grain size is stable [1–3]. The experimental finding [4, 5] that prior deformation at superplastic strain-rates does not alter the mechanical properties also seems to suggest that strain is an unimportant variable during superplastic flow.

"Dynamic" mechanical history, however, has not been considered to date. For example, a given strain-rate of $\dot{\epsilon}_1$ may be reached in case of two nearly identical specimens by elongating them to different lengths l_1 and l_2 at cross-head speeds V_1 and V_2, respectively, such that $V_1/l_1 = V_2/l_2 = \dot{\epsilon}_1$. If Equation 1 represents an equation of state (i.e. is independent of the path by which $\dot{\epsilon}_1$ is approached) the observed stress in either case should be equal, provided necking and grain growth are absent.

Bars of chill-cast Pb–Sn–Cd ternary eutectic alloy were zone-refined using fourteen passes and subsequently rolled at room temperature to produce sheets of approximate thickness 0.8 mm. Thickness of tensile specimens, produced by stamping, varied between 0.74 and 0.86 mm although within each specimen no thickness variation was allowed. The width was constant and equal to 6.5 mm while the gauge length lay between 19.7 and 21.3 mm.

Specimens needed for a series of tests were taken from the same ingot to eliminate grain-size variation. Stability of grain size during deformation, on the other hand, was ensured by heat-

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treatment before the tests at 373 K for 1.2 ksec. The grain size in the heat-treated condition was estimated to be 3.9 μm using a Quantitative Television Microscope (quantimet). Isothermal tensile tests involving the use of the Instron Universal testing machine were carried out inside a water bath at cross-head velocities of 3.3, 6.7 and 16.7 mm ksec^{-1} at each of the three temperatures 298, 318 and 343 K.

During the tests flow of the grip regions was detected. This was taken into account by introducing a "grip-slip" correction. If L_I is the initial gauge length and L_o and L_F the gauge length and the separation between the grip regions after the test, respectively, the correction factor Z that should be applied to the strain-rate is given by

$$Z = \frac{(L_o - L_I)}{(L_F - L_I)}$$

if a linear variation of strain-rate is assumed along the length of the specimen. Likewise, it can be shown that the correction factor Z' for the stress is equal to (L_o/L_F). Therefore, the true stress, σ_t and the true strain-rate, $\dot{\epsilon}_t$, are to be evaluated as

$$\sigma_t = \sigma_{obs} \times Z' \quad (2)$$

and

$$\dot{\epsilon}_t = \dot{\epsilon}_{obs} \times Z, \quad (3)$$

where σ_{obs} and $\dot{\epsilon}_{obs}$ are the uncorrected values of the stress and strain-rate, respectively, evaluated assuming uniform deformation. As necks formed during superplastic flow are very diffuse [1–3] ignoring their presence does not introduce serious errors in the computed values of σ_{obs} and $\dot{\epsilon}_{obs}$. It is necessary, however, to take into account local deformation if pronounced necking is observed during the tests.

The results of the tension tests, presented in Table I, clearly show that on the basis of both the corrected and uncorrected values the stress is not a single valued function of strain-rate. Instead, the stress corresponding to a given strain-rate increases with increasing cross-head velocity/strain (as at a higher cross-head speed the given strain-rate is reached after larger strain, increasing the cross-head velocity automatically increases the strain). Therefore, it follows that for Equation 1 to be strictly valid the cross-head velocity/strain at which the strain-rate is evaluated should be specified, in addition to the grain size of the material and the temperature of deformation.

However, as pointed out earlier, extremely large elongations lead to negligible work-hardening in case of superplastic flow [1–3]. Therefore, the conventional role of strain in increasing the flow stress may be ruled out. Alternatively, the increase in stress at a given strain-rate with cross-head velocity/strain may be interpreted in terms of the increase in the "apparent viscosity" of the medium. A recent rheological model envisages superplasticity to arise from the viscous flow of grain boundaries surrounding essentially non-deforming grains [6]. This picture reduces the superplastic alloy undergoing deformation to a condensed particulate system in which the particles (grains) get dragged along by the flowing boundaries. In this case the resistance to flow may be expected to increase with cross-head speed on account of the greater number of particle (grain) collisions per unit time. This picture is also consistent with the experimental results presented below.

The possibility of local deformation and structural changes (grain growth) contributing to the observed increase in stress with cross-head speed/strain was also examined. In the present experiments necking was virtually absent. In any case, limited local deformation (arising from very diffuse necks) cannot result in more than 100% increase in stress (Table I).

An examination of post-deformation microstructures by optical microscopy revealed that grain growth was negligible. Further, grain growth could be seen to be unimportant from the following results: at 298 K when $\dot{\epsilon}_t$ was 1.2×10^{-4} sec^{-1}, σ_t values of 9.13 and 15.07 MN m^{-2}, respectively, were obtained corresponding to two cross-head speeds 6.7 and 16.7 mm ksec^{-1} (Table I). The time intervals before the evaluation of strain-rate in these cases were 2.268 and 1.494 ksec, respectively. If temperature induced grain growth was responsible for the observed increase in stress, σ_t should have been greater for the test performed at 6.7 mm ksec^{-1}. Optical microscopy, on the other hand, indicated that strain-induced grain growth was insignificant.

The experimental results of Fields and Stewart [7] also suggest that the cross-head velocity may influence the magnitude of stress corresponding to

TABLE I

Temp. (K)	$\dot{\epsilon}_t$ (sec^{-1})	Cross-head speed (mm $ksec^{-1}$)	σ_t (MN m^{-2})	Time* (ksec)	Uncorrected values	
					$\dot{\epsilon}_{obs}$ (sec^{-1})	σ_{obs} (MN m^{-2})
298	1.2×10^{-4}	3.3	7.75	0	1.6×10^{-4}	9.81
		6.7	9.13	2.268	1.9×10^{-4}	13.24
		16.7	15.07	1.494	1.3×10^{-4}	16.75
318	1.2×10^{-4}	3.3	2.21	0	1.7×10^{-4}	2.76
		6.7	3.18	3.288	1.6×10^{-4}	3.97
		16.7	3.76	5.958	1.4×10^{-4}	4.31
343	1.1×10^{-4}	3.3	0.85	0	1.6×10^{-4}	1.12
		6.7	1.89	3.990	1.4×10^{-4}	2.28
		16.7	2.08	5.712	1.5×10^{-4}	2.63

*Indicates the time interval between the attainment of steady state and of strain-rate evaluation.

a given strain-rate. However, their interpretation in terms of "strain hardening and strain softening" resulting from the thermo-mechanical history of the specimens is somewhat dubious in view of the finding that in materials with stable grain size superplastic deformation is not accompanied by work-hardening (see above). Instead, their results can be accounted for by the present approach where the increase in stress with cross-head is attributed to the increased particle (grain) collisions per unit time.

Thus, it is evident that Equation 1 is not strictly valid for superplastic alloys. Alternatively, the results indicate that in addition to the grain size and the temperature of deformation the cross-head velocity/strain at which the stress–strain-rate relation is evaluated should also be specified for Equation 1 to be rigorously satisfied.

Rheological analysis of isothermal superplastic deformation is available for both situations when (a) the duplex nature of the alloy is taken into account and (b) the material is treated as a homogeneous continuum [6]. For the latter case, within the steady state

$$\sigma = N^2 f V e^{-(f/M)t} \quad (4)$$

where N is the number of grains per unit volume, f the friction factor, V the velocity of the cross-head, M the *average* mass of a grain and t the time at which the stress, σ, is evaluated (in [6] due to a typographical error N^2 in Equation 4 appears as N). The Appendix of [6] reveals that experimental results justify the assumption of the rheological analysis that f is constant for constant V.

From Table 1 of [6] it also emerges that f/M and hence f increases with V (M is constant for constant grain size). This is a consequence of the finding reported in the previous section that the stress at a given strain-rate increases with increasing cross-head speed. It is natural that f, which is a measure of the apparent viscosity of the medium, should increase with an increase in the number of particle (grain) collisions per unit time.

Further, the rheological analysis [6] has predicted that in constant velocity isothermal tests, f/M is equal to the strain-rate at which superplasticity sets in. For the Pb–Sn–Cd eutectic alloy tested at 343 K and a cross-head velocity of 8.3 mm $ksec^{-1}$ an average f/M value of 3×10^{-5} sec^{-1} has been obtained [6]. Moles [8] has estimated that in the above material at 343 K, consistent with the theoretical prediction, superplasticity (as defined by a sharp increase in the slope of the $\log \sigma - \log \dot{\epsilon}$ plot) is first encountered at a strain-rate of about 5×10^{-5} sec^{-1}.

Thus the experimental results presented above and the Appendix of [6] are seen to be complementary.

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K. A. PADMANABHAN
Department of Metallurgical Engineering,
Banaras Hindu University,
Varanasi-221005, India

M. D. C. MOLES
G. J. DAVIES
Department of Metallurgy and Materials Science,
University of Cambridge,
Cambridge, UK

Orientation of bismuth films on mica

During the growth of bismuth films on sodium chloride substrates, two orientations, (001) and (012), are reported to be developed with equal probabilities, and suitable changes in the deposition conditions result in a predominant (001) or (012) orientation [1–4]. The azimuthal orientation of the crystallites will be such that the [100] direction remains parallel to the [100] or [110] directions of the substrate [2, 3]. However, when deposited on mica cleavages, the (001) orientation is dominant over (011) and (012) orientations with the [100] direction making an angle of 30° with respect to the [010] direction of mica [1]. The different orientations mentioned are essentially of finished films and depend more on the kinetics of the development of the individual nuclei rather than the initial orientation of the crystallites. This seems reasonable as the conditions of condensation have a greater influence on the orientation of the deposits than the material of the substrate, and in spite of the difference in the planar symmetry of the substrate surfaces on which the deposits are formed, the character of bismuth epitaxy is basically the same on mica as well as on alkali halides [1]. In this letter we report the appearance and the elimination of the (012) orientation of the bismuth deposits on mica cleavages as an effect of the deposition parameters.

Observations were made on bismuth films, 600 to 700 Å thick, vapour-deposited onto mica cleavages heated to temperatures in the range 25 to 130° C. The rate of deposition of the vapour flux was maintained at 40 to 50 Å sec^{-1}. The films were examined by transmission electron microscopy after stripping from the substrates.

It is observed that all the films deposited at 25° C were polycrystalline but showed a clear (001) texture (Fig. 1a). At higher temperatures (50 to 100° C) the films were made up of single crystalline grains of (001), (011) and (012) orientations with various azimuthal orientations, but when the temperature was above 100° C, the (011) and (012) orientations were absent and the films were (001) oriented except for the mis-

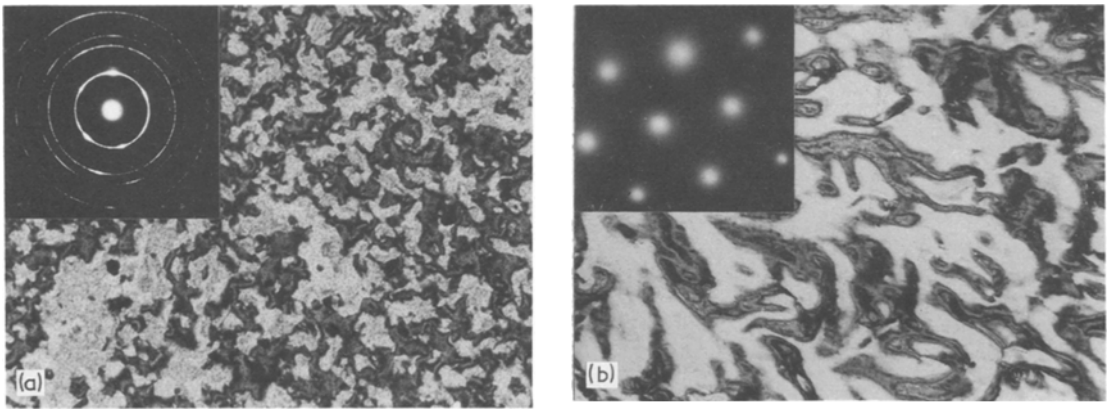

Figure 1 Bismuth films deposited onto mica substrates (a) at 25° C and (b) 130° C.

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