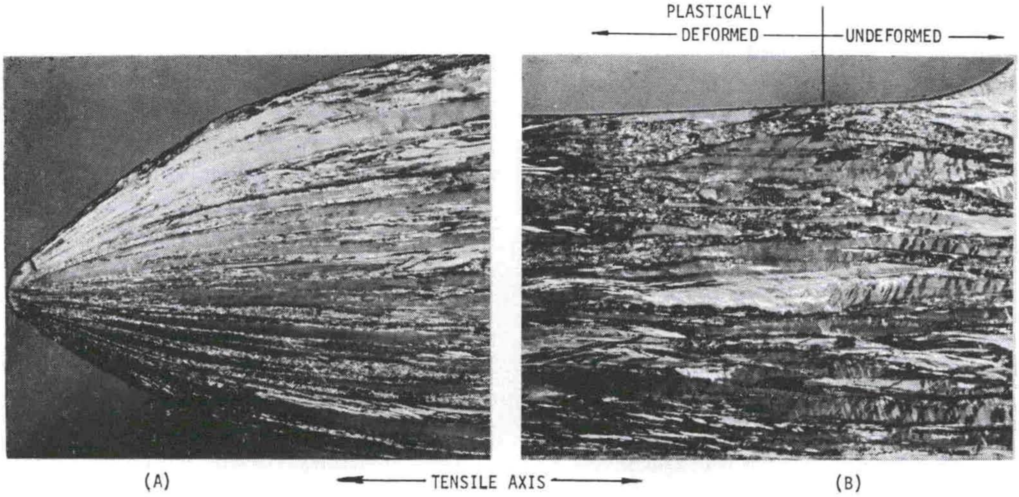

FIG. 14. The microstructure of 9% Sn–bal Bi specimens tested to fracture at 15.0×10^8 N/m^2: (a) showing failure by rapture, 59 ×, Unetched, Polarized Light. (b) same specimen as in (a) above, but area shown is of material in the vicinity of the shoulders. Note to transition from an indistinct to a pronounced grain structure at the apparent boundary between plastically deformed and undeformed material, 50 ×, Unetched, Polarized Light.

DISCUSSION

Ductility at atmospheric pressure

Inherent ductility at ambient temperatures and atmospheric pressure is 100 per cent for pure tin and virtually zero for pure bismuth. As an initial assumption, it would appear reasonable that ductility would be some continuous function, decreasing as the volume fraction of Bi is increased. In contrast, the alloy system behaves in a manner quite different from that expected.

In previous work with tin–binary alloys having up to 20 wt.% Bi, Alden(11) noted that specimens were somewhat brittle when annealed at 75–100°C, which he attributed to the embrittling effect of Bi particles along grain boundaries. It was observed in this current study that considerable Bi precipitation also occurred along specific crystallographic planes of the Sn phase. The low ductility of Sn rich alloys is a manifestation of the presence of these Bi particles and results in the following fracture sequence. First, particle–matrix separation occurs along favorably oriented grain boundaries. As the tensile stress is increased, these separations join to form an intergranular crack. Further propagation then occurs by either further grain boundary fracture or (more probably) by travel along a favorably oriented collection of precipitate particles situated along some crystallographic plane in the tin. Eventual link-up of cracks to form the macroscopic fracture surface would be accomplished by the rupture of "bridges" of Sn-rich solid solution. The decrease in ductility with increasing Bi concentration in the Sn-rich alloys is attributed to the closer spacing of the Bi particles, which results in a more continuous plane of weakness.

As the composition is changed so as to approach the eutectic composition, a substantial rise in ductility is observed. This rise, which is on the order of 40 per cent, appears to be due to a decrease in grain size. Grain size was determined through linear intercept methods, and the average grain diameter of the 90 per cent Sn alloy was approximately 1.2×10^{-1} cm. In the eutectic structure, the interphase distance was approximately 7.6×10^{-5} cm. The difference in grain size (which is of several orders of magnitude) is considered the primary contributing factor for the disparity. Crack initiation occurs by both the cleavage fracture of the Bi and failure at the Sn–Bi interface. However, even though there are more available initiation sites in eutectic vs the Sn-rich alloys, the mean free path before the cracks encounter the ductile Sn phase is much less. Thus, more strain is required to extend cracks through the Sn.

The rapid drop in ductility at Bi levels above the eutectic composition results from the controlling effect of large areas of the brittle Bi phase.

The most probable mechanism for crack nucleation is the intersection of twins with grain boundaries (i.e. the same mechanism as observed in pure bismuth), with a possible assist from grain boundary sliding, as $T = 0.93T_m$. Although evidence of cavity formation along grain boundaries is indicative of grain boundary sliding, none were seen, and rarely was metallographic evidence of separation along grain boundaries observed. This lack of evidence leads to the opinion that grain boundary sliding is a minor mode of crack nucleation, and the predominant mechanism to be the nucleation of cracks at the intersections of twins and grain boundaries.

Effects of superimposed hydrostatic pressures

Ductility in terms of reduction in area as a function of pressure at ambient temperatures is shown for pure Bi and Sn–Bi alloys in Figs. 2(a) and (c). While data reported by Pugh(4) appears to show equivalent levels of ductility to occur at lower pressures, the data given was for a Bi–Ag alloy rather than for pure Bi. The anomalous behavior of Sn–Bi alloys as reported by Livshits *et al*,(10) which was ascribed to the character of the pressure-melting temperature curve for this alloy(14) was not duplicated. However, due to the sensitive response of ductility with composition observed to occur for this alloy system (Fig. 8), small composition differences, which would be present in the cast alloys used by Livshits *et al.*(10) in their investigation, could allow their observed shifts in ductility to occur.

Superimposed hydrostatic pressure will not affect the initiation stage of cleavage fracture except in a small if not negligible way.(15) However, if the effect of a superimposed pressure were to result in counteracting (i.e. decrease) the normal stress by the magnitude of the pressure, crack propagation would be impaired.(7) This would effectively retard intergranular fracture and cleavage. It is apparent from examination of Fig. 7(a) that concomitant with an increase in pressure is an increase in the number of twins and a decrease in the number of cracks observed. It is proposed that the retarding of crack propagation by the application of a superimposed hydrostatic pressure will result in the increase in ductility observed by allowing deformation by twinning to proceed to an extent not possible at atmospheric pressure. Also, there exists in the literature some evidence for the enhancement of deformation of bismuth by slip and grain boundary sliding when exposed to superimposed hydrostatic pressure.(16)

Also, an effect of pressure would be to collapse voids forming on a microscopic scale. Since the pressure to collapse a void in a given material is given as approximately two-thirds the yield strength(12) of the material and the tensile strength of tin is given(13) as $1.4 \times 10^4 N/m^2$ (2100 psi), it would be expected that pressure would have a strong effect on the formation, growth and coalescence of voids in the Sn matrix. Fractographs, Figs. 14(b) and (c), taken at the apparent ultimate fracture surface show dimpling, with the size of dimples decreasing and the frequency of occurrence increasing as the pressure increases, indicating that the effect of pressure will be to reduce void growth, probably by reducing the rate of vacancy diffusion coupled with the tendency to collapse voids at pressures equal to two-thirds the yield stress and to decrease the normal stress contributions to fracture which would tend to promote failure by mechanisms dependent on shear strain.

It should be noted that the value for the BDTP for pure bismuth $6.5 \times 10^8 N/m^2$ (6.5 kb) is approximately $2 \times 10^8 N/m^2$ (2 kb) higher than a value for the BDTP derived from results reported by Pugh for a bismuth 2 per cent silver alloy(9) and is taken as an indication of the sensitivity of the BDTP to impurity levels. Also of note is the shifting of the BDTP to $11.5 \times 10^8 N/m^2$ (11.5 kb) for the as-received (as cast) materials, which is taken to indicate the effects of microstructure (columnar vs equiaxed) and possible casting defects (such as internally oxidized areas etc.), in addition to any chemical effects introduced by the remelting and subsequent extrusion. It is readily apparent that parameters describing the initial conditions with respect to purity and structure would have a large effect on subsequent mechanical behavior.

While twinning is recognized as the predominant mode of deformation at atmospheric pressure,(17,18) the suggestion by Davidson *et al.*(7) that superimposed hydrostatic pressure will affect the normal stress component of the basic Griffith relationship(19) by decreasing the normal tensile stress by the magnitude of the pressure, thereby impairing or suppressing crack propagation by cleavage or intergranular modes, is considered to be especially relevant for pure bismuth as bismuth obeys a critical normal stress to fracture law.(20) Therefore, since the propagation of microcracks would be suppressed by application of a superimposed hydrostatic pressure, the propensity towards deformation by twinning should be enhanced, giving rise to an increase in ductility. At pressures greater than $5 \times 10^8 N/m^2$ (5 kb), grain boundary effects and slip have been observed in pure Bi.(16,21) It is quite possible that the effect of pressure on the deformation characteristics of bismuth, when combined with the effect on the normal tensile stress component and subsequent effects on crack propagation, gives rise to the abrupt ductile–brittle transition observed.

The ductility response of Sn–Bi alloys subjected to superimposed hydrostatic pressures is considered to be a manifestation of the shift of the brittle-to-ductile transition temperature (BDTT). However, at or near atmospheric pressure, this effect may not be