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**The significance of strain weakening and self-annealing**

**in a superplastic Bi-Sn eutectic alloy processed by**

**high-pressure torsion**

Chuan Ting Wang1, Yong He1, Terence G. Langdon2,3\*

1School of Mechanical Engineering, Nanjing University of Science & Technology,

Nanjing 210094, China

2 Materials Research Group, Department of Mechanical Engineering,

University of Southampton, Southampton SO17 1BJ, U.K.

3Departments of Aerospace & Mechanical Engineering and Materials Science,

University of Southern California, Los Angeles, CA 90089-1453, U.S.A.

**Abstract**

 A cast Bi-Sn eutectic alloy was processed by high-pressure torsion (HPT) at room temperature and stored at room temperature for durations of up to 91 days in order to investigate the effect of self-annealing. The HPT processing produces grain refinement but hardness measurements show there is strain softening with lower microhardness values than in the initial as-cast material and with hardness values that decrease with increasing amounts of imposed torsional strain. This softening is attributed to a loss of precipitates within the Sn and Bi phases during the processing operation. In self-annealing at room temperature, the microhardness increases significantly due to reprecipitation and there is also a minor increase in grain size with increasing time of storage. It is demonstrated by tensile testing that the HPT-processed Bi-Sn alloy exhibits superplastic behavior with elongations of up to >1000% after storage for 35 days and with an associated strain rate sensitivity close to ~0.5. Grain boundary sliding plays an important role in superplastic flow and it is shown that maximum sliding occurs on the Bi-Bi interfaces where this is consistent with estimates of the coefficients for grain boundary diffusion in the Bi-Sn alloy.

*Keywords*: Bi-Sn alloy; grain boundary sliding; hardness; high-pressure torsion; superplasticity.

Corresponding author: Terence G. Langdon (langdon@soton.ac.uk)

## Introduction

Processing through the application of severe plastic deformation (SPD) provides an opportunity for achieving exceptional grain refinement to the submicrometer or even the nanometer level [1-4]. Currently, the two major SPD procedures are equal-channel angular pressing (ECAP) where a bar or rod is pressed through a die constrained within a channel [5] and high-pressure torsion (HPT) where a disk is subjected to a high applied pressure and concurrent torsional straining [6]. Of these two procedures, HPT has an advantage in producing both smaller grain sizes [7,8] and higher fractions of grain boundaries having high angles of misorientation [9]. An attractive feature of the SPD-processed metals is that they generally, but not always, exhibit high strength and, because of the very small grain sizes, they have a potential for achieving superplastic elongations when testing in tension at elevated temperatures.

Although high strength is anticipated in ultrafine-grained (UFG) materials because of the Hall-Petch relationship [10,11], careful experiments have shown that in some materials the SPD processing may produce a weakening rather than a strengthening [12]. For example, when using ECAP with a spray-cast Al-7034 alloy the material became weaker after processing by ECAP because the processing led to a partial loss of the hardening metastable η′ phase [13]. The situation for metals processed by HPT is more complex because in practice the processing may produce a strengthening, a weakening or a combination of both.

A recent report provided a detailed summary of the various possibilities that occur in the hardening of metals when processing by HPT [14]. First, most metals exhibit a strengthening after HPT such that the hardness increases with increasing strain but ultimately saturates at a relatively low torsional strain. This behavior was designated “Without recovery” because the hardening occurs in the absence of any significant recovery effects. Second, some metals may exhibit a strain hardening in the very early stages of processing but then significant softening and microstructural recovery followed by saturation at a lower strain. This type of behavior was designated “With recovery” and it denotes a situation where there is some microstructural recovery after the initial hardening. This behavior was first identified in samples of high-purity Al [15] and later confirmed also in high-purity Mg [16] and Zn [17]. Third, the hardness may decrease with increasing strain and finally saturate at a much lower level. This is designated “With weakening” and it occurs when the material weakens in the absence of any evidence for strain hardening. There was an early report of this behavior for the Zn-Al eutectoid alloy [18] and the effect was interpreted by transmission electron microscopy observations showing that processing by HPT at room temperature (RT) reduces the distribution of rod-shaped precipitates of stable hexagonal close-packed Zn which are contained within the Al-rich grains in the initial unprocessed condition [19,20]. Later experiments confirmed this weakening in the Zn-Al alloy [21-26] and there were also reports of similar weakenings in the Pb-Sn eutectic alloy [23,24,27], the Bi-Sn eutectic alloy [28], various Al-Zn alloys [29-32] and high-purity Pb, Sn and In [17]. Although all of these results refer to the processing of metals exclusively by HPT, care must be exercised when combining different processing procedures because it was shown that metals may either strengthen or weaken when processed alternately by the two procedures of ECAP and HPT [33].

For materials exhibiting a weakening behavior in HPT, it is important to determine whether the UFG microstructures and the low hardness values are retained even after self-annealing through storage at RT. Self-annealing experiments were conducted on the Zn-Al alloy [24] and the Pb-Sn alloy [24,27,34] and these results show consistently that the alloys gradually harden with increasing times of storage.

Following a detailed review of the experimental data available to date, the present investigation was initiated to provide comprehensive information both on the strengthening/weakening behavior during processing by HPT of a Bi-42% Sn eutectic alloy and on the effect of subsequent self-annealing of the as-processed material by storage at RT. This material was selected because very early work in 1934 used a similar near-eutectic alloy of Bi-44% Sn and demonstrated the first reported example of true superplastic flow in a polycrystalline material with an elongation of ~1950% when pulling in tension at RT [35].

## Experimental material and procedures

The Bi-42% Sn eutectic alloy was supplied by Wochang Nonferrous Metal Materials Ltd. (Dongguan, PRC) in the form of a cast ingot with approximate dimensions of 55 × 35 × 250 mm3. Thin disk samples were machined from the as-cast ingot with diameters of 10 mm and these disks were ground to final thicknesses between 0.80 and 0.85 mm.

The HPT facility consisted of massive upper and lower anvils with each anvil having a circular depression on the inner face with a diameter of 10 mm and a depth of 0.25 mm. For the HPT processing, the disk was placed in the depression on the lower anvil and this was raised into position and subjected to a pressure of 6.0 GPa. Torsional straining was then conducted at RT by rotation of the lower anvil. All HPT processing was performed under quasi-constrained conditions in which there is some restricted outflow of material around the edge of the sample during processing [36,37]. Various total strains were imposed on the disks by processing through numbers, *N*, of 1, 5 and 10 revolutions under a constant rotation speed of 1 rpm. Following HPT, self-annealing was conducted by storing disks at RT for various times up to a maximum of 91 days. The absolute melting temperature, *T*m, of the Bi-Sn eutectic alloy is 412 K [38] so that ambient temperature is ~0.7 *T*m and this means that diffusive processes occur rapidly during storage.

After HPT processing, disks of both the as-cast and the HPT-processed alloy were polished to 1600 grit, then to 1 µm using a diamond suspension and finally a vibratory polisher was used to remove any scratches with a 0.04 μm colloidal silica suspension. Focused ion beam (FIB) was employed to investigate the nature of the Sn particles within the Bi phase after HPT processing and storage at RT using an ion beam voltage of 30 kV and a current of 50 pA. Microhardness values were recorded along selected diameters on the polished surfaces using an FM-1e Vickers hardness tester with a load of 50 gf and separate dwell times of 10 s for each indentation. Since the HPT disks are very small, two miniature tensile specimens with gauge lengths of 1 mm were prepared using electro-discharge machining from symmetrical off-center positions within the HPT disks as described earlier [39]. These miniature specimens were tested in tension to failure at room temperature using an Instron testing machine operating under conditions of constant cross-head displacement with initial strain rates from 1.0 × 10-4 to 1.0 × 10-‑2 s-1. In order to obtain information on the nature of any superplastic flow, a single disk was processed by HPT through 10 turns, stored at RT for 35 days and then a tensile specimen was cut from the disk, the surface was polished and it was pulled to an elongation of 30% for subsequent microscopic examination.

The microstructures of selected samples were observed with a scanning electron microscope (SEM) JEOL JSM-7001 F operating at a voltage of 15 kV with the samples etched using a solution of 25 ml H2O, 5 ml HCl with a concentration of 37 % and 5 g of NH4NO3. The SEM was equipped with an electron backscatter diffraction (EBSD) detector and a TSL orientation imaging system and the results were analyzed using Orientation Imaging Microscopy (OIM) software. All of the EBSD data were collected at a working distance of 15 mm using a sample tilt of 70°.

## Experimental results

*3.1 Microhardness values after HPT processing and after HPT with self-annealing*

The individual values of the Vickers microhardness, Hv, taken along randomly selected diameters on each disk sample are plotted in Fig. 1(a) as a function of distance from the centers of the disks for the samples taken through 1, 5 and 10 turns where the upper dashed line denotes the hardness value of 25.2 Hv recorded for the initial as-cast condition prior to HPT processing. These values were recorded within 2 h after the HPT processing and the effect of self-annealing is shown by the hardness values plotted in Fig. 1(b) for the same samples after storage at RT for 14 days.

Several conclusions may be drawn from inspection of Figs 1(a) and (b). First, the microhardness values of all samples decrease significantly after HPT processing by comparison with the initial as-cast condition. This strain weakening in HPT is similar to the trends reported earlier for the Zn-Al eutectoid alloy and the Pb-Sn eutectic alloy [23] and the effect of self-annealing is also similar to results documented for these two alloys [24]. However, it is important to note that a two-phase eutectic or eutectoid structure is not a sufficient requirement to attain a strain weakening effect in HPT processing since similar hardness measurements on an Al-33% Cu eutectic alloy showed strain hardening which effectively matches the behavior in most single phase metals [40]. Second, the HPT-processed samples generally show higher hardness values in the centers of the disks with lower values at the edges and this is especially apparent after 1 turn without any self-annealing. This variation is a direct consequence of the change in strain across the disk since the shear strain, *γ*, is given by the relationship [41]:

  (1)

where *N* is the number of rotations, *R* is the distance from the center of the disk and *h* is the thickness of the sample. Third, the hardness of all HPT-processed samples increases after storage at RT and in some parts of the disk this increase is rather substantial. For example, after 10 turns of HPT processing the sample has a hardness of ~7 Hv at the edge of the disk in Fig. 1(a) but the hardness value in this area increases to ~17 Hv after storage for 14 days. These measurements show, therefore, that the microstructure of the Bi-Sn alloy produced by HPT is unstable and rapidly recovers during storage at RT.

To provide a more detailed assessment of the self-annealing effect, ten individual microhardness values were recorded at about 2 mm from the center of each disk and the averages of these measurements were plotted against the numbers of days of storage at RT as shown in Fig 2. Inspection of these data shows that the microhardness drops to about 8 Hv after HPT processing but thereafter it increases rapidly during storage. Thus, these results provide a clear demonstration of the necessity for recording meaningful hardness measurements immediately after the HPT processing. It is apparent that the hardness values increase to ~17-20 Hv after storage for about 7 days and then there is a gradual increase to a final saturation hardness of about 22 Hv after storage for 40 days. Ultimately, there appears to be no significant difference in the hardness values attained after long-term storage for the samples processed through 1 to 10 turns since all samples have a hardness of ~20 Hv after storage for 21 days. Careful measurements gave a saturation hardness of 22.3 ± 0.6 Hv in the 5 turns sample after storage for 70 days.

*3.2 Microstructural evolution after HPT processing and after HPT with self-annealing*

Evidence of microstructural refinement and recovery after HPT processing and self-annealing is shown in the SEM images in Fig. 3 where (a) is the microstructure in the initial as-cast Bi-Sn alloy and the other images show the microstructures after processing through 10 HPT turns and then storing at RT for (b) 1, (c) 7, (d) 15 and (e) 91 days, respectively: for ease of comparison, all images are shown at the same magnification. In the as-cast condition in Fig. 3(a) the alloy has a lamellar structure, the two phases have area ratios of about 6:4 and in this etched condition, where the Sn phase is roughened during preparation, the lighter phase is Sn and the darker phase is Bi. The phase spacing was estimated as ~3.5 ± 0.7 μm and, since no boundaries were visible within each phase, this value corresponds to the initial grain size.

After HPT processing and storage at room temperature for 1 day as shown in Fig. 3(b), the microstructure is very significantly refined and both the Pb and Sn phases are essentially randomly distributed with a more homogeneous distribution of phases by comparison with the as-cast material and with very few Bi precipitates visible within the Sn phases. By identifying the individual grain boundaries within each phase, measurements gave an average grain size of ~0.94 ± 0.18 μm in this condition and this value, recorded after 1 day, corresponds reasonably to the microstructure immediately after HPT processing. There is a similar microstructure after storage for 7 days in Fig. 3(c) but the grain size is then slightly larger at ~1.27 ± 0.31 μm and after storage for 35 days in Fig. 3(d) the grain size is ~1.37 ± 0.21 μm. These microstructures and the associated measurements demonstrate that during storage at RT the two phases of the HPT-processed Bi-Sn alloy grow separately and this is a direct consequence of the rapid diffusion at this relatively high homologous temperature.

The microstructure after 91 days of storage is shown in Fig. 3(e) and it is similar in appearance to the structure after storage for 35 days except that the measured grain size has increased to ~1.81 ± 0.60 μm. Figure 4 shows a higher magnification of the microstructure after 10 turns and storage for 91 days where Fig. 4(a) reveals the presence of two distinct phases formed by the agglomeration of grains and at this higher magnification the individual grain boundaries are clearly visible within each phase without etching. There is also evidence for the presence of many fine Bi particles within the Sn-rich phase in the as-cast condition and some pitting holes are visible in the Bi-rich phase in Fig. 4(b) because the Sn particles tend to etch away during the preparation of samples for SEM. Nevertheless, the numbers of Sn particles visible within the Bi phase are less than the numbers of Bi particles visible within the Sn phase after etching.

The evidence from these microstructures and the hardness measurements in Fig. 2 suggest that the HPT processing produces a reasonably steady-state condition after storage for about 35 days. Therefore, in order to obtain a reasonable set of experimental data, most of the subsequent experiments were performed on either the as-cast alloy or on the Bi-Sn alloy after HPT processing and storage for 35 days at RT. These measurements therefore avoided any differences that may arise from grain growth during the early stages of storage at RT immediately after the HPT processing.

Figure 5 compares the microstructures of the as-cast Bi-Sn alloy recorded by EBSD as (a) a phase map and (b) an orientation map and similar phase and orientation maps are shown after HPT through 10 turns and storage for 35 days at RT in (c) and (d), respectively. These images were taken on the surfaces of the disks at distances of ~2 mm from the disk centers. In Fig. 5 the unit triangles are shown for the Bi and Sn in the right column where the colors of the grains correspond to the appropriate orientations within the triangles. Thus, the Bi phase is shown in red while the Sn phase is shown in green and there are many fine Bi particles visible in the Sn phase which is consistent with the microstructural appearance in Fig. 3(a). The as-cast Bi-Sn alloy also has a very strong texture as shown in Fig. 5(b) with the Sn phase having a {100} crystallographic direction and the Bi phase having a crystallographic direction close to $\left\{1\overbar{1}00\right\}. In $addition, many annealing twins are visible in the hexagonal close-packed (hcp) Bi phase. After HPT processing and storage for 35 days, the grains of the Sn phase are not easily identified because Bi precipitates are now present due to reprecipitation within the Sn phase and the presence of these scattered hard particles makes it difficult to prepare a flat surface by polishing. Nevertheless, the results in Fig. 5(d) show that the orientations of the Bi phases become essentially random. Therefore, it is concluded that the HPT processing and the imposition of a high hydrostatic stress break up the strong annealing texture and the lamellar structure associated with the initial as-cast Bi-Sn alloy and thereby transform the structure into arrays of randomly oriented grains having essentially an equiaxed configuration.

*3.3 Flow properties after HPT processing and after HPT with self-annealing*

Figure 6 shows plots of true stress versus true strain for tests conducted at RT (298 K) using (a) the as-cast alloy without HPT processing and (b) the alloy processed by HPT through 10 turns and then stored for 35 days at RT. These curves are similar to those recorded in other samples of this alloy at various testing temperatures up to 353 K and they show that a reasonably steady-state condition is attained prior to failure. For all testing conditions within this temperature range, the elongations achieved in the as-cast material were significantly lower than those associated with true superplastic flow which, by definition, requires elongations to failure of at least 400% [42].

Examples of the as-cast samples are shown in Fig. 7 after pulling to failure for testing temperatures of (a) 298 and (b) 353 K where the upper samples are in the initial untested condition and all other samples show clear evidence for necking within the gauge lengths. By contrast, excellent superplastic flow was achieved in the alloy after processing through 10 turns of HPT and then storing for 35 days at RT and the specimens after fracture are shown in Fig. 8 after testing in tension at the same temperatures of (a) 298 and (b) 353 K. Thus, there is an excellent superplastic elongation of 1220% at the lowest strain rate of 1.0 × 10-4 s-1 at 298 K and at the higher temperature of 353 K there is a superplastic elongation of 1470% at the highest strain rate of 1.0 × 10-2 s-1 where this latter result confirms the occurrence of high strain rate superplasticity in this alloy [43]. Inspection shows that these highly superplastic samples pull out to failure without any evidence for necking within the gauge lengths and this is consistent with the requirements for true superplasticity [44]. The high elongations achieved in these samples after storage at RT for 35 days are due to the development of an initial equiaxed array of grains as shown in Fig. 5(d) where this contrasts with the lamellar structure which is present in the initial as-cast condition as shown in Fig. 3(a).

An examination of Fig. 8 shows that the highest elongation occurs at the slowest strain rate at 298 K but at the fastest strain rate at 353 K. This displacement of the optimum conditions to faster strain rates at higher temperatures was first reported in very early experiments on the Zn-22% Al eutectoid alloy and it arises because the stress-strain rate relationships are displaced to faster strain rates with increasing temperature [45]. The samples in Fig. 8 show also that larger superplastic elongations are achieved at the higher testing temperature and, as noted also in an earlier report [46], this is because less time is available at these faster strain rates for cavities to develop, grow and interlink along the internal boundaries to produce cavitation failure.

For convenience, the experimental elongations over a wide range of strain rates are plotted in Fig. 9 for the as-cast samples and the samples processed through 10 turns, stored for 35 days at RT and then tested in tension at (a) 298 and (b) 353 K, respectively. The lower dashed lines delineate the elongations for the as-cast material where the failure strains are essentially independent of strain rate. For the stored samples, the elongations decrease at the faster testing strain rates at 298 K in Fig. 9(a) but they increase at the fastest strain rate at 353 K in Fig. 9(b) where these trends are generally consistent with the expectations for nanocrystalline materials [47].

Figure 10 shows plots of flow stress against strain rate at three different testing temperatures for (a) the as-cast Bi-Sn alloy and (b) after HPT for 10 turns and storage at RT for 35 days prior to tensile testing. Thus, the as-cast alloy has a low strain rate sensitivity of *m* ≈ 0.23 at all temperatures from 298 to 353 K and this is consistent with the low elongations recorded in Fig. 7. By contrast, the samples processed through 10 turns and stored for 35 days give a strain rate sensitivity of *m* ≈ 0.54 except at the fastest strain rates close to 10-2 s-1 at 298 K where the value is reduced to *m* ≈ 0.23 and, as shown in Fig. 8(a), the material is no longer superplastic.

*3.4 The microstructural characteristics of superplastic flow in the Bi-Sn alloy*

Since it is well-established that the grains remain essentially equiaxed during superplastic flow, even when the elongations to failure are exceptionally high, it is reasonable to anticipate that the rate-controlling flow process in these superplastic samples is grain boundary sliding [48]. It is appropriate, therefore, to critically examine the Bi-Sn samples for direct microstructural evidence of the occurrence of sliding and this may be achieved by examining the polished surfaces of samples after tensile testing to low elongations. Although it is apparent that surface grains are subjected to fewer constraints than the grains contained within the interiors of samples, early measurements using internal markers in creep testing demonstrated unequivocally that identical grain boundary sliding offsets may be recorded from markers in the specimen interior and in the plane of the surface after tensile testing [49,50].

An example is shown in Fig. 11 where a selected area of the polished surface is shown (a) after HPT processing for 10 turns and storage for 35 days without tensile testing and (b) after HPT processing, storage and then pulling in tension to an elongation of 30% at RT using an initial strain rate of 1.0  10-4 s-1: the vertical arrow in (a) shows the direction of the tensile axis. Since the sample in Fig. 11 was only fine polished without etching, the lighter grains are the Bi-rich phase and the darker grains are the Sn-rich phase. Although the elongation in Fig. 11(b) does not constitute superplastic flow, it is apparent from Fig. 8(a) that this testing condition provides the capability of producing an exceptional superplastic elongation of ~1220% when pulling to failure.

A close comparison of Figs 11(a) and (b), and other similar photomicrographs, provides clear evidence for the relative displacements of adjacent grains in grain boundary sliding at, for example, the Bi-Sn boundaries between the grains numbered 1 and 2 and between grains 2 and 3. There is also an example of the opening of a large sharply-defined cavity along the Bi-Bi boundary between grains 4 and 8 and a grain boundary crack between grains 9 and 10, where these observations demonstrate that sliding occurs easily between the Bi grains. The opening up of surface cavities in this way is a well-established feature of conventional superplastic flow and it leads, with increasing strain, to the emergence of internal grains at the specimen surface to account for the increase in surface area as the specimen pulls out in tension [51,52]. It is concluded from these and similar observations at other surface areas that sliding occurs at the Bi-Sn and Sn-Sn interfaces but there is maximum sliding at the Bi-Bi interfaces.

**4. Discussion**

*4.1 Significance of strengthening and weakening during SPD processing and the effect of short-term-annealing*

When bulk solids are subjected to processing by SPD procedures such as ECAP or HPT, the grain size is reduced and the materials generally exhibit a strengthening because of the Hall-Petch relationship [10,11]. Nevertheless, in some materials the grain refinement produces a weakening which is associated with additional mechanisms that occur in the material due to the high hydrostatic stresses imposed in the processing operation. The present experiments show there is a significant weakening on the application of HPT to the Bi-Sn eutectic alloy as shown in Fig. 1(a) and this means the behaviour matches similar weakening reported earlier for the Zn-Al eutectoid and the Pb-Sn eutectic [23]. For the present investigation, the Bi-Sn alloy contains an Sn phase which is significantly decorated with Bi precipitates [53] and this is confirmed directly in Fig. 4(b). In addition, Sn particles are present within the Bi phase and pitting holes are widely observed after etching as shown also in Fig. 4(b). It is concluded that, as in the Zn-Al eutectoid where the weakening was attributed to the removal of Zn from within the Al-rich grains during processing [19,20], the present initial weakening is due to the breaking of many of the precipitates under the very high shearing stresses during the processing operation and the subsequent hardening during long-term storage is due to a reprecipitation process.

The effect of self-annealing is important after SPD processing because it defines the stability of the UFG microstructure. In the Bi-Sn alloy the hardness increases with storage time at RT as shown in Figs 1(b) and 2 and this hardening is similar to results reported earlier for the Zn-22% Al and Pb-62% Sn alloys [24,27]. In addition to an increase in hardening, there is also a small increase in grain size, by less than a factor of 2, from ~0.9 μm initially to ~1.4 and ~1.8 μm after storage for 35 and 91 days, respectively.

There is some evidence supporting this hardening effect in Fig. 3 because it appears that Bi particles may reprecipitate within the Sn phase and Sn particles may reprecipitate within the Bi phase during storage at RT. Direct confirmation of this reprecipitation is given by measurements reported in the Appendix and contained within the Supplementary Material documenting the average sizes of the Sn particles after HPT processing and long-term storage. Specifically, it was difficult to measure the sizes of the Bi particles because of their small size and wide distribution but the Sn particles were clearly defined and their average sizes were measured as ~134 ± 55 nm for the as-cast alloy without HPT processing and then after HPT as ~75 ± 24 nm after storage for 7 days, ~122 ± 88 nm after storage for 35 days and ~130 ± 78 nm after storage for 90 days. These results demonstrate that the Sn particles within the Bi phase are initially fragmented by the high pressures in HPT processing but subsequently there is a reprecipitation during long-term storage at RT. The second phase particles may be dissolved into the matrix due to mechanical alloying as a result of the severe plastic deformation, where such features have been widely observed in two-phase alloys even with very low mutual solubility such as Fe/Cu and Cu/Co. Such a mechanical alloying process was attributed to the Gibbs-Thomson effect [54-56].

In HPT processing the amount of continuous shearing is very large and the second phase particles may be broken down to the nano-scale. Such a capillary effect on the nano-particles may produce significant changes in the phase diagram with the formation of a supersaturated solution [57,58]. During HPT processing, as the pressure of 6.0 GPa was applied to the sample the interdiffusion between Bi and Sn was significantly restrained even while new grain boundaries and vacancies were introduced by HPT, and when the high pressure was released the second phase particles may undergo reprecipitation under the ambient temperature of ~0.7 *T*m.  Additional information on reprecipitation, obtained from X-ray diffraction (XRD) using a step-scanning diffractometer, is given in the Supplementary Material.

Grain boundary coverage between two solid phases has been observed in several two-phase alloys, both in equilibrium and strain conditions [59-62]. It was observed that in the melt state of a two-phase alloy above the eutectic temperature there is both complete and incomplete coverage whereas at temperatures below the eutectic temperature only incomplete grain boundary coverage was observed. These results are similar to the Bi-Sn alloy in the present investigation, as shown in the microstructure of the as-cast Bi-Sn alloy in Fig. 3(a) where the alloy has a typical duplex structure such that each phase forms a branch-like structure with the gaps filled by the other phase. During large strain processing by HPT, many lattice dislocations are formed and absorbed by the grain boundaries leading to an increasing grain boundary energy. Large numbers of non-equilibrium boundaries are formed containing both structural and extrinsic dislocations and there is a complete coverage of these boundaries where the grains of one phase are surrounded by the other phase. It is clear from Fig. 3(b) that many Bi grains become essentially isolated islands surrounded by Sn grains and there are also isolated Sn grains surrounded by Bi grains. These observations demonstrate that a complete coverage of the solid grain boundaries occurs during HPT processing. Conversely, during the annealing process at room temperature this complete coverage transforms into an incomplete coverage where Bi grains connect with other Bi grains, and similarly for the Sn grains, as shown in Fig. 3(c-e).

*4.2 Significance of boundary sliding in the superplastic alloy*

From the flow stress data in Fig. 10(a), the strain rate sensitivity of *m* ≈ 0.2 in the as-cast alloy corresponds to a stress exponent of *n* ≈ 5 and this represents conventional flow where the rate-controlling mechanism is intragranular dislocation climb [63] so that the elongations are relatively low as shown in Fig. 7. By contrast, Fig. 8 shows that high elongations are achieved over a wide range of testing conditions after storage of a 10 turns sample for 35 days and in this condition the strain rate sensitivity is *m* ≈ 0.54 in Fig. 10(b) which corresponds to *n* ≈ 2. In practice, grain boundary sliding in superplasticity must be accommodated by intragranular slip to prevent the development of voids between the adjacent grains but with the slip occurring in an oscillatory manner on different slip systems so that it makes no net contribution to the overall strain. There are now several experimental investigations showing the occurrence of limited intragranular slip in highly superplastic metals [64-66].

A theoretical model was developed for superplasticity in which grain boundary sliding is controlled by the rate of accommodation by intragranular slip and this leads to a strain rate, $\dot{ε}$, which is given by a relationship of the form [67]

$ \dot{ε}= \frac{AD\_{gb}Gb}{kT} \left(\frac{b}{d}\right)^{2}\left(\frac{σ}{G}\right)^{2}$(2)

where *D*gb is the coefficient for grain boundary diffusion (= *D*o(gb) exp (−*Q*gb/*RT*), where *D*o(gb) is the frequency factor for grain boundary diffusion, *Q*gb is the activation energy for grain boundary diffusion, *R* is the gas constant and *T* is the absolute temperature), *G* is the shear modulus, **b** is the Burgers vector, *k* is Boltzmann’s constant, *d* is the grain size, *σ* is the flow stress, the exponents of the inverse grain size and the stress are both equal to 2 and *A* is a dimensionless constant having a value of ~10. This stress exponent of *n* = 2 corresponds to the measured strain rate sensitivity of *m* ≈ 0.5 over the superplastic range in Fig. 10(b) and provides confirmation that superplastic flow occurs by grain boundary sliding in the Bi-Sn alloy. This is also consistent with other comprehensive analyses of superplasticity in materials processed by ECAP and HPT [68].

Inspection of photomicrographs after pulling to low elongations as in Fig. 11 demonstrates that maximum sliding occurs on the Bi-Bi interfaces but with less sliding occurring on the Bi-Sn and Sn-Sn interfaces. This is similar to the results from earlier experiments where for the Pb-62% Sn alloy [69] and the Zn-22% Al alloy [70] there was a maximum sliding on the Sn-Sn and the Zn-Zn interfaces, less sliding on the Pb-Sn and the Zn-Al interfaces and no sliding on the Pb-Pb and the Al-Al interfaces for these two alloys, respectively. Since it follows from eq. (2) that superplasticity depends upon the rate of grain boundary diffusion, these results were explained by noting through calculations that maximum sliding occurs on those interfaces having the highest values of δ*D*gb where δ is the width of the grain boundary which is taken as ~2**b**. Thus, for these two alloys it was shown that δ*D*gb(Sn) > δ*D*gb(Pb) and δ*D*gb(Zn) > δ*D*gb(Al), respectively, which is consistent with maximum sliding on the Sn-Sn and Zn-Zn interfaces [70].

It is difficult to make a similar comparison for the Bi-42% Sn eutectic alloy because very little information is available for the diffusion coefficients for the Bi crystalline lattice. Nevertheless, it follows from earlier calculations [70] that the appropriate diffusion term for the Sn-Sn boundaries is given by [71]

 δ*D*gb = 3.22 × 10-15 exp (−40.0/*RT*) m3 s-1 (3)

where the activation energy is in kJ mol-1 and it follows that for the Sn-Sn boundaries at 298 K

 δ*D*gb(Sn) = 3.15 × 10-22 m3 s-1 (4)

For Bi, a very early report [72] was taken to estimate an activation energy for lattice diffusion in bismuth of *Q*𝓵 ≈ 77 kJ mol-1 [73] where this estimate was based on using a proportional correlation between the activation energy for lattice diffusion and the melting temperature of the metal. Although this approach provides only an approximate value for *Q*𝓵, extensive analyses for many metals show that it is a reasonable procedure when a direct experimental measurement of the activation energy is not available [74]. Using published diffusion data for Bi at a temperature of 773 K [75] and assuming similar pre-exponential factors for lattice and grain boundary diffusion, the lattice diffusion coefficient in Bi is estimated as ~5.4 × 10-9 m2 s-1 so that, taking *Q*𝓵 ≈ 77 kJ mol-‑1 at this temperature, *D*o(gb) = 8.63 × 10-4 m2 s-1. Following the procedure developed earlier [70], taking *Q*gb ≈ 0.6*Q*𝓵 gives a value for Bi at 298 K of *D*gb = 6.88 × 10-12 m3 s-1. The primary slip system for Bi at RT is $\left(111\right)<1\overbar{1}0>$ so that **b** = 4.52 × 10-10 m [76]. Finally, this leads to a value for the Bi-Bi boundaries of

 δ*D*gb(Bi) = 6.23 × 10-21 m3 s-1. (5)

Therefore, the calculations show that δ*D*gb(Bi) > δ*D*gb(Sn) and this indicates that the Bi-Bi boundaries are preferential sites for the occurrence of grain boundary sliding by comparison with the Sn-Sn boundaries where this calculation is consistent with the experimental observations shown in Fig. 11. Unfortunately, no diffusion data are available at present to permit a similar calculation for the Bi-Sn interphase boundaries.

Finally, it is necessary to examine the extent of superplasticity in this alloy. The maximum elongation to failure achieved in tensile testing at RT was 1220% at a strain rate of 1.0 × 10-4 s-1 after storage for 35 days. This is significantly smaller than the elongation of ~1950% reported in very early experiments on the Bi-44% Sn alloy when testing at RT [35] and it is lower also than the elongation of 1325% reported in the Bi-Sn eutectic alloy when testing at RT at a strain rate of 1.0 × 10-5 s-1 after processing by ECAP for 8 passes and storing for 40 days [77]. In principle, it is well established that the elongations to failure are generally larger when the gauge lengths of the tensile specimens are reduced [78,79]. Nevertheless, the elongations attained in the miniature tensile specimens cut from HPT disks are usually smaller than anticipated because these specimens have reduced thicknesses, typically of the order of ~0.6 mm after the HPT processing, and there are then insufficient numbers of grains contained within the sample cross-sections in order to accommodate the development of exceptionally high elongations. Therefore, it is anticipated, and is confirmed by the experimental results, that these HPT samples will exhibit reduced elongations by comparison with samples having regular cross-sections. This same problem of the occurrence of reduced ductilities in HPT samples was noted also in a recent evaluation of superplastic flow in Al-Mg-Sc alloys [80].

**5.** **Summary and conclusions**

1. Experiments on a Bi-42% Sn eutectic alloy show that processing by HPT leads to grain refinement but also to a weakening due to the breaking of second phase particles which are present in the as-cast material. Subsequent self-annealing at room temperature increases the hardness for storage up to about 20 days due to a reprecipitation effect but thereafter the hardness remains reasonably constant.
2. The alloy exhibits good superplastic elongations after storage for 35 days with maximum elongations of >1000%. The measured strain rate sensitivity in the superplastic region is ~0.54 which is consistent with grain boundary sliding as the rate-controlling mechanism.
3. Microstructural observations at low elongations within the superplastic regime show that sliding occurs preferentially on the Bi-Bi boundaries and this is consistent with an estimate of the relevant diffusion coefficients for diffusion in the Bi-Sn alloy.

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**Appendix**

*Direct evidence for the breaking and subsequent reprecipitation of Sn particles within the Bi phase*

The cross-section of a disk sample was milled by FIB so that the Sn particles became visible. A typical FIB-milled surface is shown in Fig. S1 in the Supplementary Material where Bi particles are homogeneously distributed within the Sn phase and Sn particles are homogeneously distributed within the Bi phase. In practice, it was difficult to measure the Bi particles because of their small size and distribution but it is reasonably easy to take measurements of the average sizes of the Sn particles. Figure S2 shows a cross-sectional micorstructure of the initial as-cast Bi-Sn alloy and Figs S3-S5 show cross-sectional microstructures after processing through 10 HPT turns and then storing at RT for 7, 35 and 91 days, respectively. As described in detail in the Supplementary Material, the average sizes of the Sn particles within the Bi phase were measured for each condition.

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**Figure Captions**

**Figure 1** Variation of Vickers microhardness with distance from the centers of the disks before and after HPT processing: (a) within 2 hours after HPT processing and (b) after HPT processing and storage for 14 days at room temperature.

**Figure 2** Vickers microhardness measured 2 mm from the disk centers versus numbers of days of storage at RT for the as-cast alloy and after HPT processing through 1, 5 and 10 turns.

**Figure 3** Microstructures of Bi-Sn samples (a) in the as-cast condition and after HPT processing for 10 turns and storage at RT for (b) 1 day, (c) 7 days, (d) 35 days and (e) 91 days.

**Figure 4** Microstructures of Bi-Sn sample after HPT processing for 10 turns and storage at RT for 91 days (a) without etching and (b) after etching.

**Figure 5** Microstructures of Bi-Sn samples by EBSD: (a) phase map and (b) orientation map of as-cast sample; (c) phase map and (d) orientation map after HPT processing and storage at RT for 35 days.

**Figure 6** True stress-true strain curves at different strain rates at RT for (a) as-cast condition and (b) after HPT processing for 10 turns and storage for 35 days.

**Figure 7** Appearance of specimens of as-cast alloy after testing to failure at different initial strain rates for tests conducted at (a) 298 K and (b) 353 K.

**Figure 8** Appearance of specimens after HPT processing for 10 turns and storage for 35 days and then testing to failure at different initial strain rates for tests conducted at (a) 298 K and (b) 353 K.

**Figure 9** Elongations after testing to failure with different initial strain rates at (a) 298 K and (b) 353 K.

**Figure 10** Flow stress versus strain rate at different temperatures for (a) the as-cast alloy and (b) the alloy processed by HPT and stored for 35 days: the slopes give the values of the strain rate sensitivity, *m*.

**Figure 11** Microstructure after processing by HPT for 10 turns and storing for 35 days (a) before and (b) after testing to 30% strain at RT: the white arrow in (a) shows the tensile direction.