Effects of wetting on the compression creep behaviour of metals containing low melting intergranular phases

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The creep behaviour of several metallic alloys containing low melting intergranular phases has been characterized in experiments performed in uniaxial compression. The alloys included Al–3% Bi–0.35% Ti, Al–8.4% Sn, Al–33% Sn, and Cu–10% Bi. By performing creep tests above and below the melting point, it was found that melting of the intergranular phase has virtually no effect on the creep behaviour of the first three materials (the aluminium alloys); they creep in a manner very similar to that of pure aluminium, and generally behave as if no second phase were present at all. On the other hand, significant changes in behaviour occur in the Cu–10% Bi alloy. Melting of the intergranular phase both enhances the rate of creep and promotes tertiary creep and failure. The creep characteristics of the materials are discussed in terms of the wetting of the liquid phase on the solid grain boundaries and the fractional area of the boundary occupied by the liquid. It is suggested that a significant portion of the grain boundary area, in excess of 70%, must be wet before the liquid influences the compression creep behaviour in a significant way.

1. Introduction

It is well established that the mechanical properties of metallic alloys containing low melting intergranular phases can be quite different at low and high temperatures, depending on whether the intergranular phase is solid or liquid [1–5]. The effects of liquid intergranular phases on the mechanical properties of metals have been widely studied, particularly in aluminium alloys [1–4]. What is usually found is that there are substantial losses in tensile ductility, impact resistance and/or fracture strength at temperatures which closely correspond to the melting of the intergranular phase. From a technological standpoint, this phenomenon is often useful in alloy design, as it frequently imparts free machining characteristics to materials [5–7].

Recent investigations have shown that the *creep* behaviour of materials can also be influenced by the presence of a liquid or amorphous intergranular phase [8–14]. In general, the effect of the liquid is to enhance the rate of creep and/or decrease the time to failure. Studies have shown that effects of the liquid can be observed in both tension and compression [12, 13], and that the enhancement of creep rates can be quite large. For example, it has been found that creep in porous potassium chloride is several orders of magnitude faster when the porosity is filled with saturated aqueous KCl solution [8, 9], and the mineral olivine has been shown to creep 2 to 5 times faster in the presence of molten basalt [14]. Similar effects have

been reported in a wide variety of materials including ceramics [11-13, 15-18], frozen soils [19-21], sea ice [22, 23], and a number of natural materials of interest to the geophysicist [14, 24-28].

Despite its apparent widespread nature, there have been very few reports of liquid enhanced creep in metals. This may be due to the fact that metallic systems which contain low melting phases are rarely used in elevated temperature service, and consequently, there has been no particular interest in studying their high temperature creep behaviour. The only study of which we are aware is one in which the compression creep behaviour of a commercially available leaded brass alloy (3% lead by weight) was characterized at temperatures above and below the melting point of lead [29]. Lead is highly insoluble in brass and is found in the microstructure as lead rich grain boundary inclusions [29]. The results of that study are summarized in Fig. 1, in which the experimentally observed steady state creep rates are plotted as a function of temperature. Also shown in the plot is a narrow band representing the range of temperature over which the boundary inclusions melt [7]. The point of interest is that there is neither a discontinuity in strain rate nor a change in the slope of the data near the melting point, thus indicating that the melting of the grain boundary phase has no effect whatsoever on the creep behaviour of this material.

As a result of this study, it was speculated that the wetting characteristics of the liquid phase on the

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Figure 1 The stress dependence of the minimum strain rates observed in a leaded brass alloy at temperatures above and below the melting point of the lead rich grain boundary inclusions (from [29]) (\Box 82.8 MPa, \triangle 70.2 MPa, \bigcirc 55.2 MPa).

solid grain boundaries may play an important role in determining whether or not liquid enhanced creep is observed. From a mechanistic standpoint, grain boundary liquid phases act to promote creep deformation by (1) providing rapid diffusion paths to enhance diffusional creep mechanisms, or (2) by providing lubricating films to enhance deformation by grain boundary sliding [8]. In either case, it can be argued that the liquid can produce a significant effect only when a large portion of the grain boundary area is wet. In the leaded brass study, the volume fraction of lead was small (about 2.1%), and the liquid wetting angle was large (about 80°) [30]. These quantities suggest, and microstructural examination revealed, that the liquid phase is distributed primarily as discrete and highly localized particles along the brass grain boundaries [29]. Consequently, a significant portion of the grain boundary area is not wet by the liquid (estimated at 91%), and the lack of a liquid phase effect is not entirely surprising.

In the current investigation, the compression creep behaviour of several other metallic alloys containing low melting intergranular phases has been characterized to further investigate the effects of wetting on liquid enhanced creep. The alloys included Al–Bi, Al–Sn, and Cu–Bi. The aluminium alloys were chosen because some aspect of their mechanical behaviour has been shown to be significantly altered by the melting of the intergranular phase [1–3]. The Cu–Bi alloy was chosen because, unlike the aluminium alloys, the liquid phase in this material is very effective in wetting the grain boundaries of the solid [30]. Overall, the wetting angles in the materials range from effectively 0° for Cu–Bi to 104° for Al–Bi, thereby



Figure 2 An optical micrograph of the structure of the Al-3% Bi-0.35% Ti alloy.

allowing for some assessment of the importance of wetting in liquid enhanced creep.

2. Experimental Procedure

2.1. Alloy preparation

The exact compositions, by weight, of the alloys studied in the investigation were Al3% Bi-0.35% Ti, Al-8.4% Sn, Al-33% Sn, and Cu-10% Bi. The compositions of the aluminium alloys were chosen to be similar to those used in prior mechanical behaviour studies [1-3]. For the Cu-Bi alloy, the choice of the composition was somewhat arbitrary, but our intention was to produce a two-phase material in which virtually 100% of the grain boundary area of the solid is wet by the intergranular phase. To the best of our knowledge, no other studies of the mechanical properties of this alloy have been undertaken.

2.2.1. AI-3% Bi-0.35% Ti

The Al-3% Bi-0.35% Ti alloy, hereafter referred to as the Al-Bi alloy, was produced by induction melting in argon and casting into graphite crucibles. The titanium addition, introduced by means of an Al-5% Ti master alloy, was intended to refine the cast microstructure. The cast ingots were extruded to a 60% reduction in area, and specimens were machined directly from the extrusions. Following machining, each specimen was annealed in argon for 5 days at 500°C. The resulting structure is shown in Fig. 2, where it is seen that the bismuth is distributed as inclusions located at the aluminium grain boundaries and within the grains themselves. For purposes of comparison to a material free of a low melting phase, samples of an Al-0.35% Ti alloy were also produced for creep testing.



Figure 3 Optical micrographs of the structures of (a) the Al-8.4% Sn alloy and (b) the Al-33% Sn alloy.

Our interest in the Al-Bi system stemmed from the observation of Roth *et al.* that the impact resistance of Al-1.5% Bi-0.35% Ti drops sharply at a temperature corresponding to the melting of bismuth [1, 2]. The alloy used in our studies had a slightly higher Bi content (3%), but was otherwise very similar.

2.2.2. Al-Sn alloys

The Al–Sn alloys were prepared using procedures similar to those for the Al–Bi alloys, with the exception that the anneal following extrusion was performed at 300° C for 2 h. Two different alloy compositions, 8.4% and 33.0% Sn, were chosen so that the effects of volume fraction of the low melting phase could be examined.

Typical microstructures are shown in Fig. 3. The tin rich phase is that which occupies less area in the micrographs. Unfortunately, we were not successful in identifying an etch which simultaneously reveals the phases and the grain boundaries, so the exact location of the tin relative to the aluminium grain structure can only be inferred from the morphology. However, based on micrographs like those in Fig. 3 and previous microstructural characterization of these alloys by other investigators [3], it is fairly clear that most of the tin resides in the aluminium boundaries, primarily at three grain junctions.

The mechanical properties of Al–Sn alloys and how they vary with temperature have been studied by Williams and Singer [3]. They have shown that both the tensile fracture strength and the tensile ductility drop sharply when the tin phase melts, with the effects being more pronounced at higher tin concentrations.

2.2.3. Cu–10% Bi

The Cu-10% Bi alloy was prepared by vacuum chill

casting. An investigation of the as-cast microstructure, which is shown in Fig. 4a, reveals that bismuth is quite effective in wetting copper, as virtually 100% of the copper grain boundary area is covered by the low melting phase. Unfortunately, this structure is not stable at the temperatures at which creep testing was to be performed, and for this reason, the material had to be annealed in argon at 400°C for 15h prior to testing to establish a thermally stable structure. The resulting microstructure is shown in Fig. 4b, in which it is apparent that a significant portion of the bismuth, which has virtually no solubility in copper, is located in the grain interiors rather than at the grain boundaries. It should also be noted that while the wetting of the copper grain boundaries by the bismuth is quite good, it is not perfect; that is, there are some areas in which solid copper-to-copper contact is maintained.

The Cu-Bi system is a classical grain boundary embrittlement system, and its mechanical properties have received a great deal of attention [31-36]. However, almost all these studies have concentrated on the behaviour of alloys containing very small amounts of bismuth, typically below the solubility limit of bismuth in copper. To the best of our knowledge, no mechanical property data are available for alloys in which the bismuth is present as a distinct, internal second phase. There are, however, reports that the mechanical behaviour of copper can be degraded in the presence of an external liquid bismuth environment [37-40]. One such study is that of Nikitin, who has found that, when immersed in liquid bismuth, polycrystalline copper creeps much faster than it does in air, both in tension and compression [40]. He has attributed this phenomenon to the Rehbinder effect [41], in which the rate of plastic deformation in a solid submersed in a liquid is enhanced because the liquid



Figure 4 Optical micrographs of the structures of the Cu-10% Bi alloy; (a) as-cast and (b) following annealing in argon at 500°C for 12h.

reduces the solid-liquid surface tension and promotes the escape of dislocations from the surface. An alternative explanation is that liquid bismuth penetrates into the microstructure along the copper grain boundaries, and the enhancement of creep results from the same mechanisms which produces it in other materials which have *internal* liquid phases. In this regard, it is notable that polycrystalline copper is highly susceptible to grain boundary penetration by liquid bismuth [38, 39]. This explanation is consistent with the experimental observations reported here.

2.3. Creep testing

Specimens for creep testing were prepared by machining right circular cylinders 12.70 mm in length and 6.35 mm in diameter from the alloyed materials. After machining, the specimens were subjected to the annealing treatments previously described. Creep tests were conducted at constant stress in compression in an apparatus constructed using design concepts reported by Donaldson and Knowles [42]. Test temperatures ranged from about 200 to 400° C and were chosen to span the range of temperature over which the inter-

TABLE I Parameters describing the wetting and melting behaviour of the intergranular phases

Material	Melting point (°C)	Dihedral angle [ref] (°)	Volume fraction (%)	Boundary area wet (%)
Al-8.4% Sn	228	58 [3]	3.3	30
Al-33% Sn	228	58 [3]	15.4	70
Al-3% Bi-0.35% Ti	270	104 [1]	0.8	15
Cu-10% Bi	270	0 [30]	9.2	95
leaded brass	318	80 [30]	2.1	9

granular phase melts. A list of the melting temperatures is included in Table I, along with other parameters which will be useful in discussing the results.

3. Results

3.1. Al-Sn

Typical creep curves for the Al-Sn alloys are shown in Fig. 5, in which the raw creep data for the Al-33% Sn alloy are plotted as strain rate against strain. The alloys exhibit normal primary creep followed by an extended period of steady state deformation. Since melting of the Al-Sn eutectic occurs at 228°C, the lower creep curve was obtained with the alloy in an entirely solid state, while for the upper two curves, the intergranular phase was molten. As will be seen later, it is significant that a prolonged period of steady state creep occurs at all three temperatures, and that the general form of the creep curves does not change when a liquid phase is present.

To demonstrate the effects of melting of the inter-



Figure 5 Creep curves for the Al-33% Sn alloy at temperatures above and below the Al-Sn eutectic (228° C) at a stress of 13.8 MPa.



Figure 6 The stress dependence of the minimum strain rates observed in the Al-Sn alloys at temperatures above and below the Al-Sn eutectic (228°C) (\Box Al-8.4% Sn, \circ Al-33% Sn), at a stress of 13.8 MPa. Also for shown for comparison are three data points for pure aluminium (\triangle) $Q_c = 136$ kJ mol⁻¹.

granular phase on the creep behaviour, the temperature dependence of the steady state creep rates for the Al-Sn alloys is plotted in Fig. 6. It is apparent from the figure that there are no changes in the creep behaviour of either alloy as a result of melting of the intergranular phase; rather, the data for each alloy fall on lines which have constant slope and exhibit no discontinuities. Also shown in Fig. 6 are the results of three tests in pure aluminium. The data fall on the same line as the Al-8.4% Sn data, indicating that this particular Al-Sn alloy creeps as if no second phase were present at all, irrespective of whether that phase is solid or molten. The 33% Sn alloy creeps at slightly higher rates, but the rates are higher by the same amount both above and below the melting point. For both alloys, the activation energy for creep is 136 kJ mol^{-1} , a value which is close to that for the creep of pure aluminium [43].

To summarize, the data in Fig. 6 clearly indicate



Figure 7 The stress dependence of the minimum strain rates observed in the Al-3% Bi-0.35% Ti alloys (O) at temperatures above and below the Al-Bi eutectic (270° C) at 15.5 MPa. Also shown for comparison are three data points for Al-0.35% Ti (\bullet), which contains no low melting phase.

that there is no effect of the melting of the intergranular phase on the compression creep behaviour of the Al–Sn alloys. In fact, with the exception that the rate of creep the 33% Sn material is slightly greater, the creep behaviour exhibited by the alloys is basically that of pure aluminium.

3.2. Al-3% Bi-0.35% Ti

The creep behaviour of the Al-3% Bi-0.35% Ti alloy is very similar to that of the Al-Sn alloys. At all temperatures, the creep curves exhibited normal primaries followed by extended secondaries. The steady state strain rates are plotted as a function of temperature in Fig. 7, where it is seen that once again, nothing out of the ordinary occurs at the melting of the intergranular phase. In addition, the creep rates of Al-3% Bi-0.35% Ti are effectively the same as those for Al-0.35% Ti, in which no second phase exists.

3.3. Cu-10% Bi

Unlike the aluminium alloys, there are dramatic differences in the creep behaviour of the Cu-10% Bi alloy associated with the melting of the intergranular phase. They show in both the form of the creep curves and the magnitudes of the minimum creep rates. In fact, the changes in creep rate that accompany melting are so large that it was difficult to establish a single stress level at which they could be measured for comparison. At stresses at which the creep rates below the melting point were large enough to be measured, the creep rates above the melting point were so fast and failure occurred in such a short period of time that quantitative measurements could not be made with any degree of certainty. On the other hand, at stresses at which the high temperature (molten boundary) behaviour could be observed, the rates of creep at low temperatures (entirely solid) were frequently less than 10^{-8} sec^{-1} , and it was impractical to let a test proceed for a long enough period of time to establish the steady state. As a consequence, it was not possible to follow the procedure used with the aluminium alloys of identifying changes in creep behaviour associated with melting by examining the temperature dependence of the steady state creep rate in plots like those of Figs 6 and 7.

As an alternative, the differences in creep behaviour



Figure 8 Creep curves for the Cu-10% Bi alloy at temperatures above and below the Cu-Bi eutectic (270°C) at a stress of 75 MPa.



Figure 9 Results of a creep test in Cu-10% Bi in which the temperature was ramped up through the Cu-Bi eutectic (270°C).

were established in two separate ways. First, in Fig. 8, two creep curves are presented – one from a test immediately below the Cu-Bi eutectic (270° C) and the other immediately above it. Note that while the test conducted below the melting point exhibits steady state creep following a normal primary, the test above the melting point shows no steady state behaviour at all; rather, a distinct minimum is observed which divides the curve into regions of primary and tertiary creep. In addition, the minimum creep rate in the upper curve is about three orders of magnitude greater than that in the lower curve. It is also notable that tertiary creep in the Cu-10% Bi alloy at temperatures above the melting point is associated with a rather dramatic failure in which specimens disintegrate into individual copper grains. Overall, this creep behaviour is in sharp contrast to that observed in the aluminium alloys, in which prolonged steady state regions and no evidence of failure were observed at strains as large as 50% (see, for example, Fig. 5).

The second illustration that melting of the intergranular phase leads to significant changes in the creep behaviour of Cu-10% Bi is shown in Fig. 9, which demonstrates the sequence of events which occurred when a specimen first crept into the steady state at a temperature of 249°C, i.e., below the Cu-Bi eutectic, after which time the temperature was slowly ramped up and through the melting point. Two curves are shown - one demonstrating how the temperature was ramped; the other, the associated changes in strain rate. What is seen is that after the ramp was begun, the strain rate increased slowly until the Cu-Bi eutectic temperature was reached, at which time there was an abrupt increase in strain rate (about an order of magnitude). Following this, a brief period was observed during which the strain rate remained relatively constant, after which the creep rate accelerated again and the specimen failed. The fact that there is a rapid increase in strain rate at a temperature which closely corresponds to the Cu-Bi eutectic and that tertiary

creep ensues shortly thereafter is a clear indication that the melting of the intergranular phase does indeed have significant effects on the creep behaviour of this material.

4. Discussion

It is clear from the results just described that liquid intergranular phases can have profound effects on the creep behaviour of some, but not all, metallic materials. Of the four alloys studied here, a significant effect was observed only in Cu–10% Bi. In the other three materials, as well as in the leaded brass alloy referred to earlier [29], no effects of the melting of the intergranular phase could be identified.

Included in Table I are estimates of the fractional grain boundary areas wet by the low melting phases, determined from optical micrographs like those in Figs 2, 3, and 4. Their values vary from a low of 9% for the leaded brass to a high of 95% for the Cu-10% Bi. It is clear from the data that the only material which exhibits liquid enhanced creep is that which has the largest fraction of its grain boundary area wet by the liquid. Thus, the data tend to confirm the previously proposed hypothesis that liquid enhanced creep is observed only in those materials in which a significant fraction of the grain boundary area is wet by the liquid [29]. Of course, wetting is promoted by small dihedral angles and large volume fractions of the low melting phase. For the Cu-10% Bi alloy, the volume fraction of the liquid phase is not large (only 9%), but this is more than made up for by the very small dihedral angle.

In this regard, it is somewhat surprising that virtually no liquid phase effect could be identified in the Al-33% Sn alloy, in which the grain boundary coverage is fairly large, about 70%. However, as shown in Fig. 10, a curious phenomenon occurs during the deformation of the Al-Sn alloys which explains why.



Figure 10 An Al-8.4% Sn specimen following deformation at a temperature above the Al-Sn eutectic showing tin extrusions at its surface. The specimen was deformed to a strain of 36%. (1 inch = 2.54 cm).



Figure 11 The microstructure of an Al-33% Sn specimen deformed to $\sim 50\%$ strain at a temperature above the Al-Sn eutectic. The undeformed microstructure is shown in Fig. 3b.

Compressive deformation is accompanied by the extrusion of liquid tin out of the microstructure to the surface of the specimen, where it solidifies as small balls upon cooling. Tests showed that this occurs only when a stress is applied, thereby ruling out "tin sweat" as the cause. As a result, the microstructures of the Al-Sn alloys were found to show substantial depletion of tin after testing. One such microstructure, an Al-33% Sn specimen deformed to 50% strain, is shown in Fig. 11. This should be compared to the starting microstructure of the material shown in Fig. 3b to appreciate just how much tin is lost. By scraping the tin from the surface, it was possible to estimate the amount of tin expelled. In a typical test, weight fractions as large as 50% of the initial tin content were not uncommon for the 33% Sn alloy. It is interesting to note that a similar extrusion phenomena have been reported for saline ice [23] and an alumina ceramic containing a glassy intergranular phase [18].

The extrusion of the liquid phase did not occur in any of the other materials, including Cu-10% Bi. Why this happens can be understood in terms of the wetting behaviour and distribution of the liquids in these solids. As shown in Table I, the dihedral angle of liquid tin on aluminium grain boundaries is about 58°. This angle is less than the critical value of 60°, below which the liquid forms a continuous network through the three grain junctions of the material (for more detailed discussions, see Smith [30] and Wray [44]). During deformation, pressure is developed in the liquid as the solid deforms, and the liquid flows out of the solid in much the same way that water is expelled from a sponge when it is squeezed. In order for this to occur, the solid must itself be fairly continuous, forming a skeleton which prevents the material from totally collapsing. An important consequence of this is that provided the liquid is free to flow, deformation is controlled primarily by processes in the solid phase, and the creep behaviour is basically that of the solid material. In addition, by virtue of expelling the liquid during deformation, the material becomes "more solid" as deformation proceeds. This, of course, is consistent with the observation that the Al–Sn alloys creep at rates very similar to those for pure aluminium (see Fig. 6).

The reason that liquid extrusion is not observed in the Al-Bi and leaded brass alloys is that the dihedral angles in these materials are significantly larger than 60°, and the liquid phase is distributed in discrete pockets from which it is not free to escape. On the other hand, the wetting is so good in the Cu-Bi alloy that there is no continuous solid network to support the load, and the material collapses into constituent solid grains with no liquid extruded. Details of the deformation process in the Cu-Bi alloy are currently being investigated and will be the subject of a future report [45].

Lastly, some comments are warranted as to why some of the mechanical properties of the aluminium alloys are degraded by boundary phase melting, while the creep resistance is not. First, and perhaps foremost, it should be noted that the mechanical properties which show degradation, the tensile strength and tensile ductility of the Al-Sn alloys [3] and the Charpy impact resistance of the Al-Bi alloy [1, 2], involve the application of tensile forces. When tensile forces are applied, liquid intergranular phases can behave like cracks, and the degradation of properties can be understood by considering the ways in which liquid phases promote fracture by acting as flaws in the microstructure [1-3]. However, the tests performed in this study were conducted only in compression, during which cracking can occur only when deformation takes place by mechanisms which lead to the development of large internal tensile stresses – mechanisms such as grain boundary sliding. Interestingly, grain boundary sliding is the dominant mechanism of deformation in the Cu-Bi alloy [45]; it can occur with relative ease because the solid structure is broken up by the nearly complete wetting of the solid by the liquid. However, in the Al-Sn alloys, grain boundary sliding is strongly inhibited by the fact that wetting is incomplete and a continuous solid network persists through the structure. Cracking is thus inhibited, and the material deforms primarily by creep within the solid phase with liquid being expelled from the solid network as deformation proceeds. In this regard, it would be interesting to repeat the experiments in tension, since substantially different behaviour could occur. It is notable that differences in the tension and compression creep behaviour of materials bearing liquid or amorphous intergranular phases have been reported for some ceramics [12, 13].

A second, but probably less important reason for the lack of liquid enhanced creep, has to do with the fact that the effects of the liquid may be significant

only at high strain rates. This hypothesis is drawn largely from experiments conducted by Roth et al. in Al-1.2% Cd-0.3% Ti [1, 2], another aluminium alloy containing a low melting intergranular phase. The behaviour of this material is, in general, similar to that of Al-3% Bi-0.35% Ti, but data have been acquired in both Charpy impact tests (relatively fast) and simple tension tests at strain rates of $1.3 \times 10^{-3} \text{ sec}^{-1}$ (relatively slow), and they show substantial differences. In particular, it has been found that while the energy absorbed during the impact tests drops off sharply from 42 to 4J as a result of the melting the intergranular phase, measures of the material's strength determined in tension tests are not nearly so greatly affected. The drop in tensile fracture strength is only from 23 to 20 MPa, and the tensile yield strength shows virtually no change at all. The only tensile property which is appreciably altered is the ductility. with the reduction in area falling from about 30% to 20%. An explanation for these observations is that the changes in mechanical behaviour associated with the melting of the grain boundary phase are strain rate dependent and become more pronounced at higher rates. Since the tests in this study were conducted at relatively low rates (less than 10^{-3}sec^{-1}), the lack of liquid phase effects in the creep behaviour of the aluminium alloys may, at least in part, be due to strain rate effects. Such a hypothesis warrants further investigation.

5. Conclusions

The results of this investigation show that, just as in other classes of materials, the presence of liquid intergranular phases in metals and alloys can influence their creep behaviour, even when tests are performed in compression. However, of the materials studied, only one, the Cu-10% Bi alloy, demonstrated any major changes associated with the melting of the intergranular phase. The enhanced minimum creep rates and accelerated tertiary creep and failure of this material are apparently due to the nearly perfect wetting of the solid by the liquid. The lack of effects in the other materials suggests that a very large portion of the grain boundary area, in excess of 70%, must be wet by the liquid before significant differences in compressive creep behaviour are observed.

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