JOURNAL OF MATERIALS SCIENCE 32 (1997) 6613–6618

Mechanical behaviour of a new dispersion-strengthened bronze

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The characteristics of a new dispersion-strengthened bronze developed by the Mixalloy system were evaluated through their mechanical properties and compared to commercial phosphorous bronze. Annealing treatment in the temperature range 400–750 °C did not produce any difference in the tensile properties of dispersion-strengthened bronze, but increasing the cold-drawing ratios resulted in a rapid increase in the tensile and yield strength. The tensile and yield strengths of cold-drawn dispersion-strengthened bronze after extrusion decreased with increasing annealing temperatures, but did not decrease greatly in the temperature range above 500 °C. The new dispersion-strengthened bronze showed superior tensile and yield strengths at high temperatures compared with commercial phosphorous bronze.

1. Introduction

Copper-base alloys have traditionally been one of the important materials in marine machinery applications because of their excellent seawater corrosion and biofouling resistance [1]. Recently, however, expensive higher strength titanium and nickel-base alloys have been increasingly utilized for good performance of current and future marine machinery, owing to the moderate strength of copper-base alloys. The application of dispersion strengthening particles, such as oxide, carbide and boride, is one method of improving the strength of copper-base alloys [2, 3]. More recently, a new material processing method, the Mixalloy process, has been developed to process a variety of innovative alloys and compositions, at low cost [4–7]. Dispersion strengthened (DS) alloys produced by the Mixalloy process, particularly those strengthened by a nano-scale refractory particle dispersion, exhibited remarkable stability at high temperatures. During the process of dispersion strengthening of alloys, the refractory particles are generated by an *in situ* chemical reaction when liquid metals are mixed, thus avoiding the tedious and time-consuming steps of incorporating or generating these particles in the matrix by mechanical milling and internal oxidation. The Mixalloy process has been very successfully applied to produce boride dispersion-strengthened copper alloys [5, 7]. However, there have been few works published on the detailed mechanical properties of a DS bronze fabricated by the Mixalloy process. This paper briefly describes the mechanical properties of a new dispersion-strengthened bronze compared with a commercial phosphorous bronze commonly used in marine machinery applications.

2. Experimental procedure

DS bronze (Cu–Sn–Ti–B) was prepared by the Mixalloy process with a chill block melt spinning [6]. The materials used in the current study are a new dispersion bronze and a phosphorous bronze, whose chemical compositions are given in Table I. When the molten materials are mixed together in a mixing chamber, boride particles are formed *in situ* (Fig. 1). The resultant mixture was then rapidly solidified using an appropriate casting apparatus. The melt-spun ribbons produced by a rapid solidification process (RSP) were pulverized, freed of reducible surface oxide by annealing in hydrogen, canned and hot extruded into cylindrical rods of 17 mm diameter. The reduction of area (RA) by hot extrusion at 750 °C was approximately 90%. After the extrusion, the annealing treatments of DS bronze were performed at temperatures between 400 and 850 °C for 1 h, followed by water quenching. Some of the extruded DS bronze was cold drawn from 22% RA to 69% RA and the cold drawn (37% RA) DS bronze was also annealed at 300, 500 and 750 °C for 1 h, followed by water quenching in order to evaluate high-temperature properties. Tensile and hardness tests were carried out to evaluate the mechanical characteristics of DS bronze at room temperature. Tensile testing was conducted at a constant displacement rate of 5 mm min^{-1} on cylindrical tensile specimens of 9 mm diameter and 25.4 mm gauge length, and yield strength was measured at the 0.2%

TABLE I Chemical compositions of DS bronze and phosphorous bronze (wt%)

	Cu	Sn	Ti	B	P
DS bronze	94.3	4.5	0.8	0.4	–
Commercial bronze	94.8	5	–	–	0.2

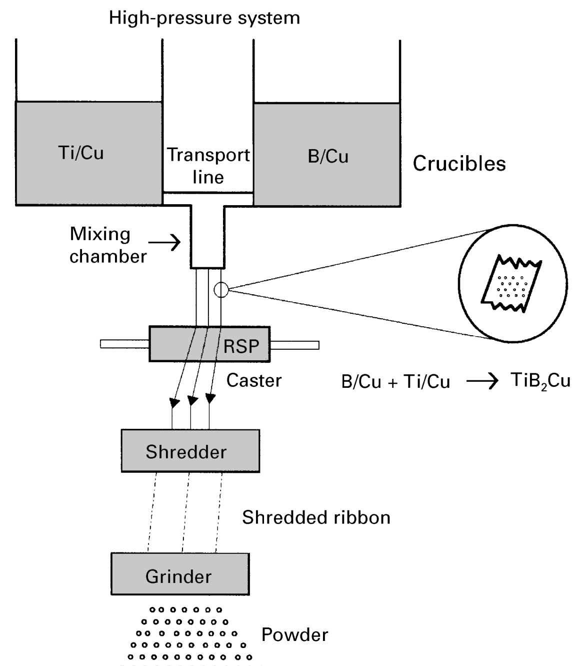


Figure 1 Schematic representation of the Mixalloy process for fabrication of DS bronze.

offset strain. Microstructure observations were made using a scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS) and the fracture surfaces of samples after the tensile test were examined.

3. Results and discussion

3.1. Stress–strain relation

Fig. 2 shows the effect of annealing conditions on the stress–strain behaviour of the DS bronze and the phosphorous bronze tested at room temperature. Because the Cu–Sn system, including DS bronze and phosphorous bronze, have a face-centred cubic (f c c) structure, smooth stress–strain curves would be expected [8]. As shown in Fig. 2, while the commercial phosphorous bronze showed characteristics of typical stress–strain curves of f c c metals and alloys, the annealed DS bronze showed a different stress–strain behaviour compared with that of commercial phosphorous bronze. A yield point was observed in as-extruded and annealed DS bronzes, except for a bronze annealed at 850 °C in Fig. 2b. This special behaviour was very similar to the yield-point phenomenon that is commonly observed in b c c metals and alloys, which could be explained using a dislocation model in a Cottrell atmosphere [9]. Considering that the atomic sizes of titanium (0.147 nm) and boron (0.097 nm) as interstitial impurity atoms are different

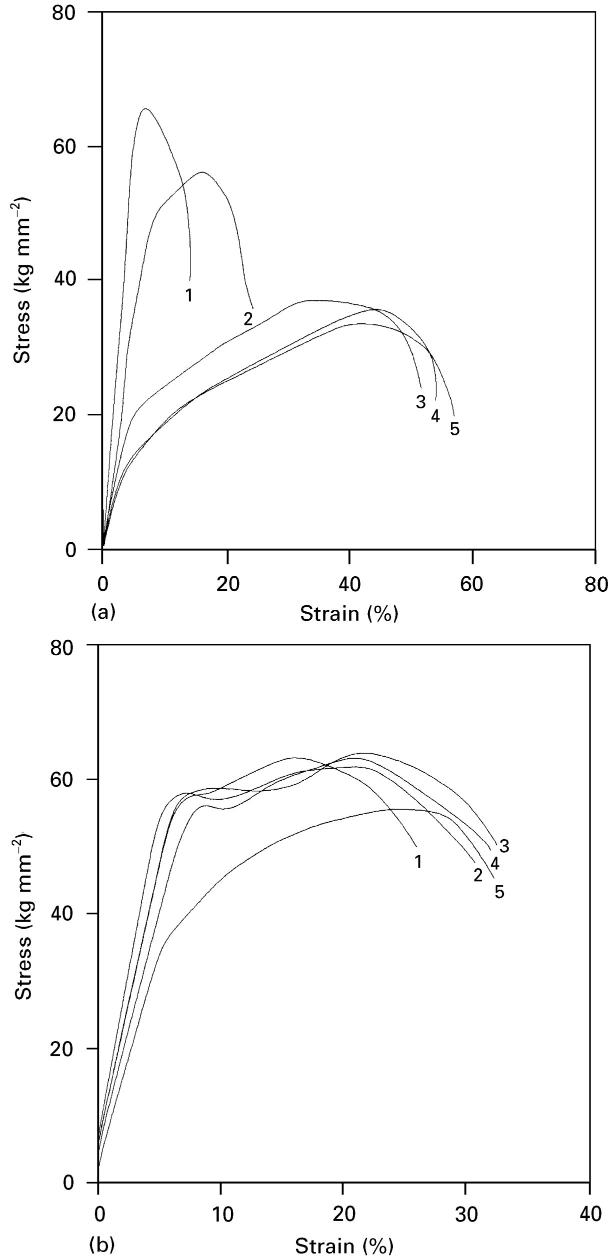


Figure 2 Stress–strain behaviour of (a) annealed commercial, and (b) annealed DS bronze at room temperature. 1, As-extruded; 2, annealed 400 °C; 3, annealed 600 °C; 4, annealed 750 °C; 5, annealed 850 °C.

from that of copper (0.128 nm), the dislocation model with association of a solute atom can be also applied to the annealed DS bronze having a yield point phenomenon, as seen in Fig. 2b. The reason for the disappearance of the yield point of the annealed DS bronze at 850 °C, is thought to be that the solute atom, boron, which was not precipitated to TiB_2, would dissolve in the bronze matrix at high annealing temperatures, 850 °C, as reported elsewhere [10].

Cold-drawn DS bronze showed another type of stress–strain curve as shown in Fig. 3. The yield -point phenomenon observed in annealed DS bronzes was not seen in cold-worked DS bronze after extrusion. The strengthening of the matrix of DS bronze by work hardening resulted in the disappearance of that phenomenon which occurred by dislocation obstruction of the Cottrell atmosphere. It was clear that the

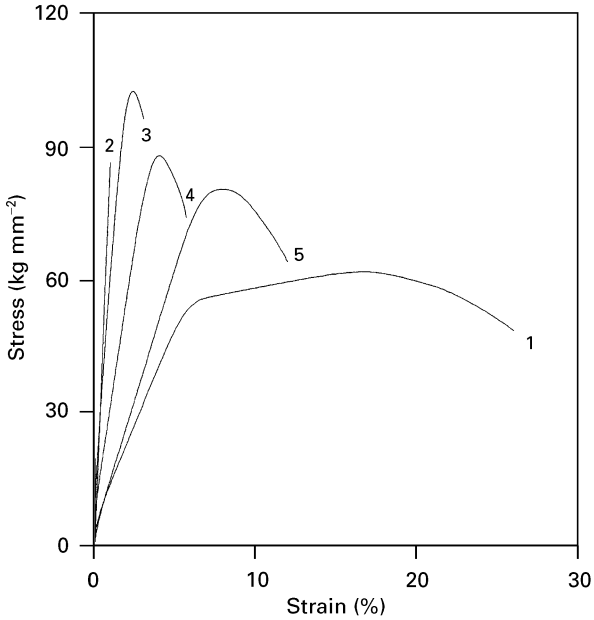


Figure 3 Stress–strain behaviour of cold-drawn DS bronze at room temperature. 1, As-extruded; 2, CD (60% RA); 3, CD (60% RA); 4, CD (37% RA); 5, CD (22% RA).

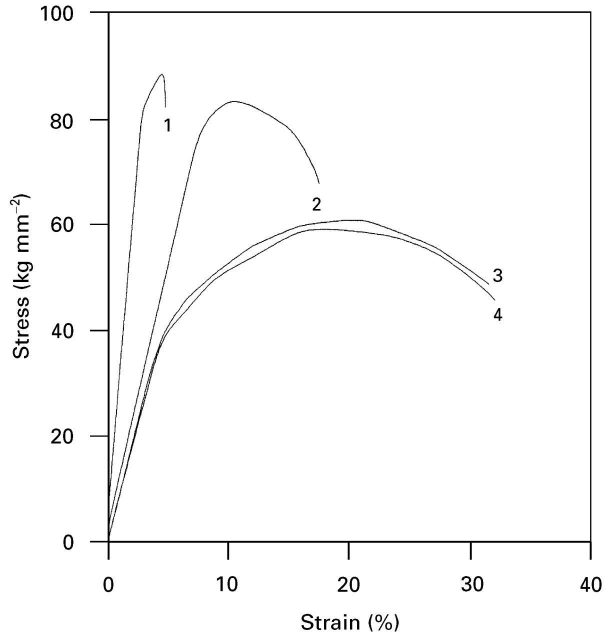


Figure 4 Stress–strain behaviour of annealed DS bronze after cold drawing at room temperature. 1, As-CD (37% RA); 2, annealed 300 °C; 3, annealed 500 °C; 4, annealed 750 °C.

excessive cold deformation above 60% induced almost nil-ductility with very high hardness and strength, as shown below in Fig. 5.

Annealing at 300 °C of cold-worked (37% RA) DS bronze provided the optimum strength and elongation, but annealing at 500 and 750 °C did not show any difference in stress–strain curves, as shown in Fig. 4. The behaviour of the annealed DS bronze was similar to that of commercial phosphorous bronze, showing low strength and high ductility as shown later in Fig. 8.

3.2. Mechanical properties

The effects of annealing temperature on the tensile and yield strengths, reduction of area, elongation and hardness of DS and phosphorous bronzes, are presented in Fig. 5. Tensile and yield strengths of DS bronze did not change with increasing annealing temperature up to 750 °C, but rapidly decreased at 850 °C. Brinell hardness, H_B, of DS also exhibited a similar behaviour to that of the tensile properties with annealing temperatures. However, the elongation of the alloy showed almost the same value, regardless of annealing treatment, while the tensile and yield strengths of commercial phosphorous bronze were rapidly decreased with increasing annealing temperature, as shown in Fig. 5a. The elongation and reduction of area of commercial phosphorous bronze were significantly affected by the annealing temperature, especially above 600 °C (Fig. 5b). Thus, the results indicate that a newly developed DS bronze which was annealed up to 750 °C had excellent mechanical properties compared with a commercial phosphorous bronze.

The variations of tensile and yield strengths, hardness, and elongation with respect to cold-drawing ratio for the cold-drawn DS bronze are shown in Fig. 6. The tensile strength of as-extruded DS bronze increased from 57.1 kg mm^{-2} to 99.5 kg mm^{-2} with increasing cold-drawing ratio. However, the tensile and yield strength of the alloy decreased above 60% cold-drawing ratio. The high cold working exhibited the very poor elongation due to the premature failure of the material, which occurred in the case of 69% cold-drawn bronze. On the other hand, the hardness increased slightly with increasing cold-drawing ratio and reached a maximum value, 104 H_B, at both 60% and 69% cold-drawn DS bronze.

The 37% cold-drawn DS bronze was annealed to evaluate the high-temperature properties at 300, 500 and 750 °C. Fig. 7 shows the effect of the second annealing temperature on several mechanical properties of the tensile test specimens for DS bronze. The properties and hardness of the bronze were almost unchanged above 500 °C, but the annealed DS bronze after cold working showed lower tensile and yield strengths compared with a cold-worked DS bronze annealed at 300 and 500 °C, as well as an as-extruded DS bronze.

3.3. Microstructures

The basic microstructure of new DS bronze containing 5% Sn is α-solid solution. In addition to tin, DS bronze fabricated by the Mixalloy system includes alloying elements titanium and boron to precipitate a boride compound (TiB_2) [5]. However, X-ray diffraction did not show the existence of any other phases except α-solid solution from the DS bronze. Although systematic studies on the particle size and volume fraction of TiB_2 have recently been carried out, the result can be related to the small amount (less than 3 vol%) of boride compound precipitated during the Mixalloy process [5, 10]. Somerkoski *et al.* found weak intensity reflections of TiB_2 phase in the X-ray

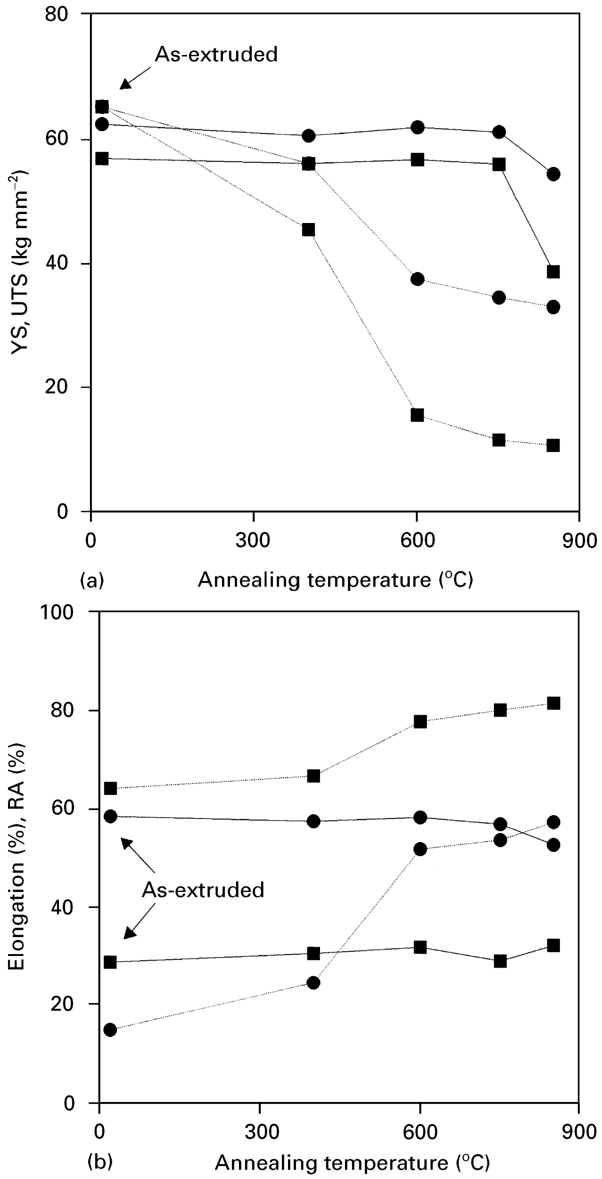


Figure 5 Comparison of tensile properties of (—) DS bronze and (---) commercial phosphorous bronze with annealing temperature. (a) (■) Yield strength and (●) ultimate tensile strength. (b) (●) Elongation and (■) reduction of area.

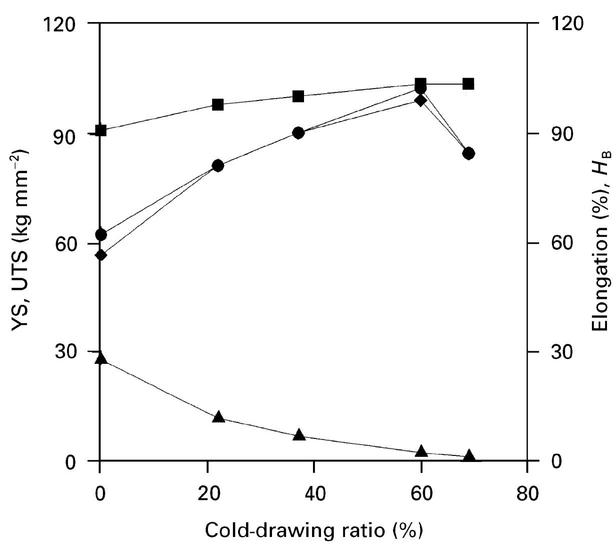


Figure 6 Tensile properties and hardness variations of DS bronze with cold-drawing ratios: (■) H_B, (◆) YS, (●) UTS, (▲) elongation.

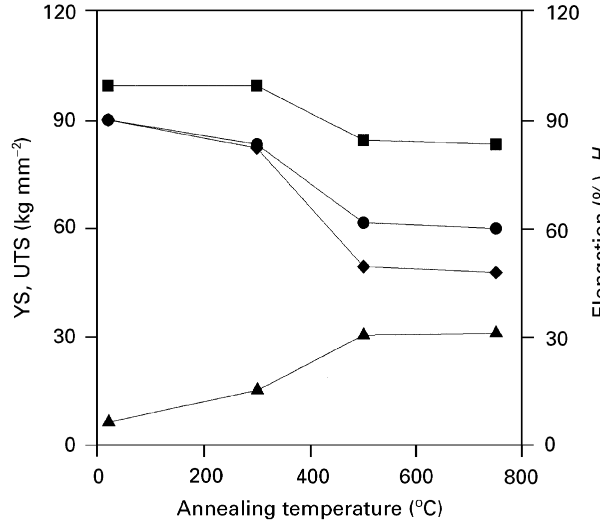


Figure 7 Tensile properties and hardness variations of cold-worked DS bronze with the second annealing temperatures: (■) H_B, (◆) YS, (●) UTS, (▲) elongation.

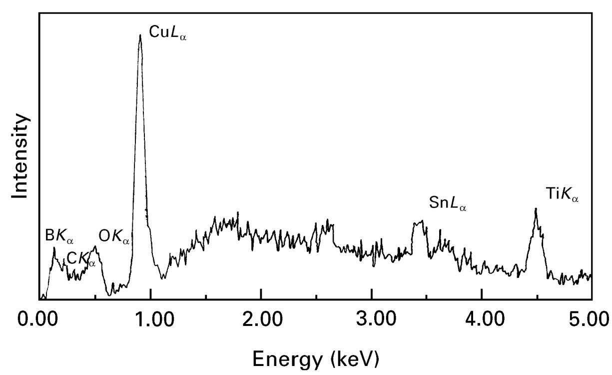


Figure 8 EDS observation of annealed DS bronze.

diffraction pattern of the Cu–Ti–B alloys produced by a molten state alloying method similar to the Mixalloy process [3]. EDS observation of annealed DS bronze showed the existence of titanium and boron peaks, as shown in Fig. 8. This boride compound was identified as TiB_2 by the qualitative analysis of titanium and boron peaks [10]. As a result of these initial analyses, a more comprehensive study is underway to determine the influence of inclusion size and spacing of TiB_2 particles in the copper matrix on the detailed mechanical behaviour.

Fig. 9 shows the variation of microstructures of DS bronze with annealing and cold-drawing conditions. The shape and size of the remaining pores after hot extrusion at 750 °C were observed in the unetched condition, as shown in Fig. 9. Most of the pores in the microstructure were relatively large in the as-extruded condition, and were found mainly along the grain boundaries. DS bronze annealed at 850 °C showed large grain size (~18 μm) with annealing twins in the grains produced by recrystallization (Fig. 9b). The annealed DS bronze after cold drawing was also recrystallized, without showing any effects of cold deformation (Fig. 9d). Cold-drawn DS bronze showed high porosity and small pores that were intensively distributed on the grain boundaries (Fig. 9c). This

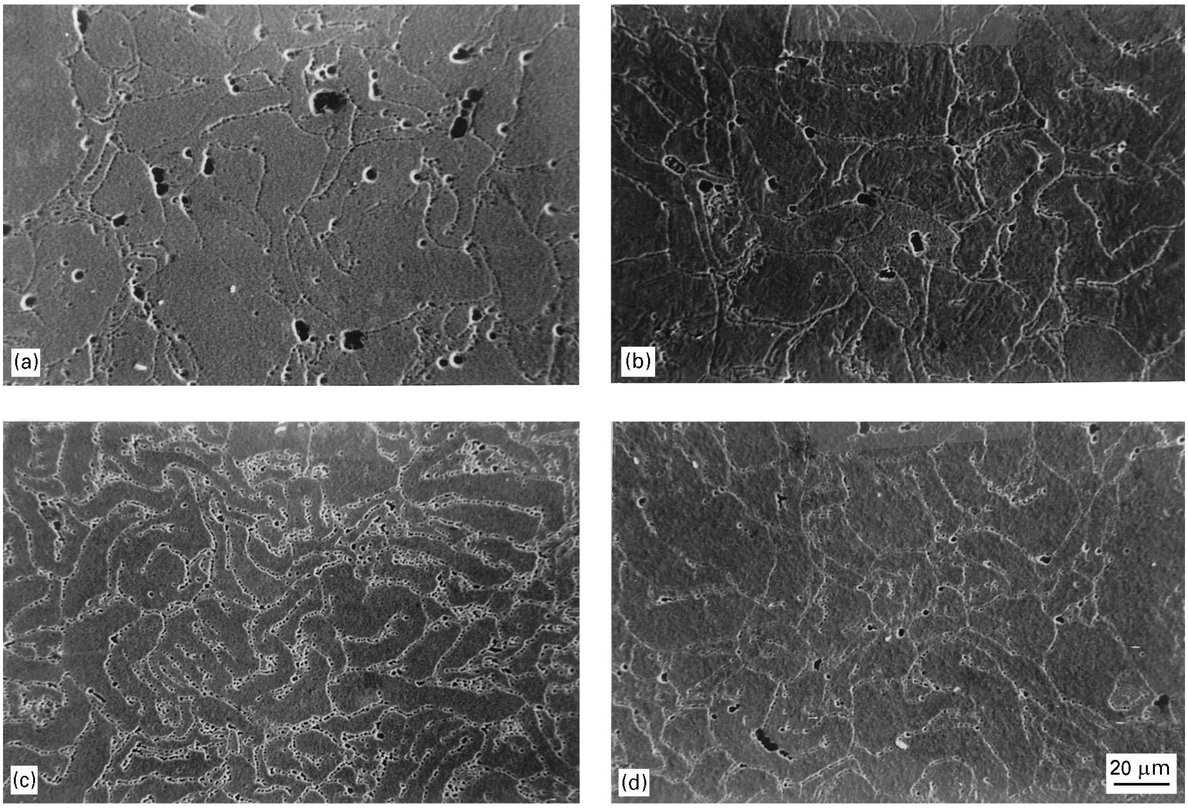
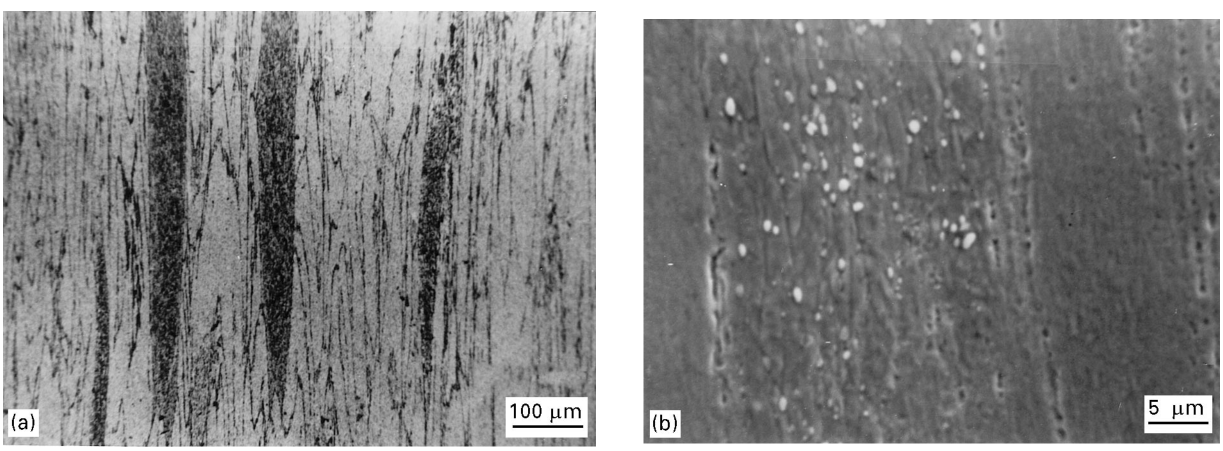


Figure 9 The shape and size of pores observed in the unetched condition by SEM. (a) As-extruded, (b) annealed at 850 °C for 1 h, (c) cold drawn (60%), (d) cold drawn (37%) and annealed at 750 °C for 1 h.



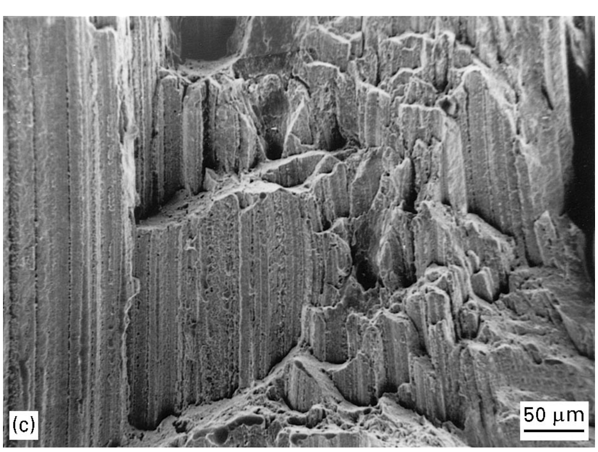


Figure 10 Elongated microstructure of the fracture surface parallel to the load direction in cold-drawn DS bronze after tensile testing: (a) elongated microstructure, (b) particles of a titanium-rich compound in the grain (dark side of (a)) (c) SEM observation of the fractured surface.

distribution of small pores on the grain boundaries would have a large effect on the fracture mode of DS bronze, as discussed below. As-extruded DS bronze (∼22µm) had a similar grain size compared to DS bronze annealed (∼18µm) at 850 °C, as shown in Fig. 9a and b, but the annealed DS bronze showed relatively lower tensile and yield strength (Fig. 5a). This would be attributed to recrystallization and the resolution of strengthening elements. The annealing treatment below 750 °C had very little effect on the grain size and the tensile properties (Figs. 2 and 5a.) The elongated microstructure of the fracture surface parallel to the loading direction in cold-drawn DS bronze after the tensile test is shown in Fig. 10a. Particles of titanium-rich compound were observed in elongated grains by SEM in Fig. 10b, and were

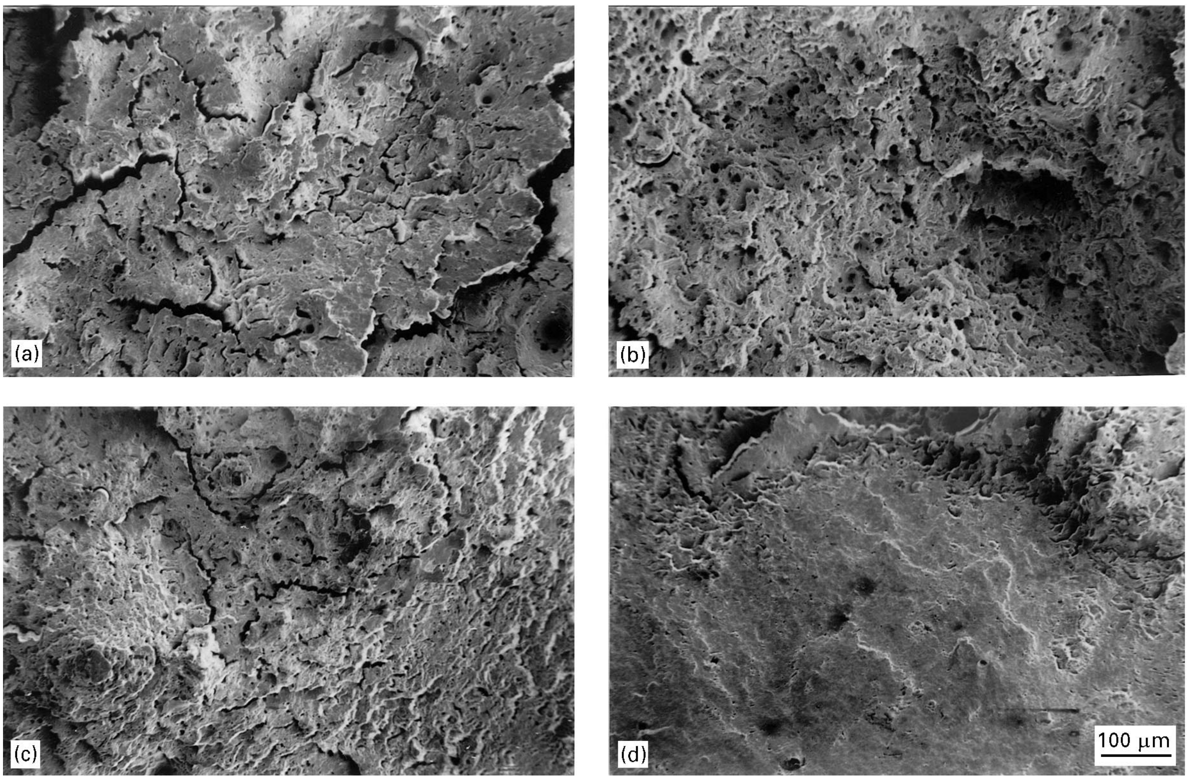


Figure 11 SEM observation of fractured surfaces after tensile testing: (a) as-extruded, (b) annealed at 850 °C for 1 h, (c) annealed at 850 °C and deformed (CD, 60%) at room temperature, (d) deformed at RT and annealed also at 750 °C for 1 h.

identified as TiB_2 by EDS, as shown in Fig. 8. Most of the titanium and boron added to DS bronze would not be precipitated as TiB_2, and some would be dissolved in the matrix. It is suggested, therefore, that the particles located on grain boundaries and pores would have a large effect on tensile properties, namely high strength with low ductility.

Fig. 11 shows an SEM fractograph of a fracture surface after tensile testing. The severely cold-drawn DS bronze, Fig. 11c, showed a different fracture mode compared with the others. The dimple mode showing some ductility was almost unobserved, but the fracture mode was not the same as a brittle fracture mode. The cracked surfaces were observed by SEM in the lateral direction, as shown in Fig. 11d. It was interesting that the fracture mode showed neither typical ductile mode nor brittle fracture mode. The cracked surface of tensile specimens after the test was similar to a splitting phenomenon. Splitting of the fracture surface of tensile specimens has been frequently observed in specimens machined from controlled-rolled plate and pipe line steels [11]. The splits in the cracked surface, which are also referred to as delamination, might be attributed to pores and titanium-rich particles partially contained in some grain boundaries, as shown in Fig. 10c.

4. Conclusion

The mechanical properties of a new dispersion-strengthened (DS) bronze fabricated by Mixalloy process were evaluated and compared with a commercial phosphorous bronze. The DS bronze showed different stress–strain curve behaviour in tensile test compared with commercial phosphorous bronze. A yield-point phenomenon, which was very similar to that of low-carbon steel, was observed in specimens as-extruded and annealed below 750 °C. When compared with a commercial phosphorous bronze, DS bronze showed superior mechanical properties at room temperature. The fracture mode of DS bronze was neither typical dimple nor brittle fracture: delamination as the fracture mode, was attributed to pores and titanium-rich particles existing along the grain boundaries. The strengthening mechanism of the DS bronze is thought to be associated with undissolved alloying elements (titanium and boron) and TiB_2 formed in the Mixalloy process.

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Received 4 December 1995
and accepted 10 March 1997