

Age hardening of rapidly quenched Al–Zr–B alloys

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Ternary alloys from the Al–Zr–B system were prepared as thin foils by a rapid quench technique. These foils were annealed isothermally as well as isochronally at various temperatures (150 to 550°C). The microstructures show that at high temperature, the grain growth is significantly retarded by the grain boundary pinning of boride precipitates. A strong age hardening is also a characteristic phenomenon in these alloys. It is found that microstructure and microhardness largely depend upon the zirconium/boron ratio of the alloy, indicating that the ratio determines the types of compounds occurring in this alloy system. It appears that in these alloys, high concentration of boron and the low ratio of zirconium/boron together yield stable precipitates at high temperatures.

1. Introduction

In recent years, many elements with very low solubility in aluminium (late transition metals, metalloids, etc.) have been extensively incorporated into aluminium alloys through rapid solidification processing in order to achieve high specific strength and good high temperature properties [1–4]. These alloys are strengthened by finely dispersed, stable intermetallic compounds that are formed during rapid solidification and/or precipitated during subsequent consolidation and processing. A typical example is seen in Al–Fe–Ce alloys [5] in which the dispersoids are coarsening resistant even at 350°C [6–8]. Less attention has been given to early transition metals as alloying elements, e.g. Group IV elements like zirconium, titanium, and hafnium. It is well known that an addition of titanium in aluminium alloys refines grains by the nucleation of α (aluminium) phase around Al_3Ti compounds [9, 10]; a proper addition of boron to titanium-bearing aluminium alloys further enhances grain refinement by forming finer Al_3Ti compounds [11–14]. A similar behaviour was observed in rapidly solidified Al–Zr–B alloys in the present experiment. In addition, adding boron to Al–Zr alloys was found to significantly improve the thermal stability, rendering Al–Zr–B alloys a potential for high temperature applications.

2. Experimental details

Al–Zr_{1.5–3.5}B_{1.5–6.0} alloys were prepared from Zr–B master alloys, 99.99% pure zirconium and 99.9% pure boron in an arc furnace under an argon atmosphere. Al–Zr_{1.5–3.5} alloys were also prepared for base data collection. The alloy buttons were splat quenched into

thin foils (20 to 40 μm thick) by the hammer and anvil technique. The foils were sealed in vacuum quartz tubings and heat treated isochronally and isothermally. Vickers microhardness measurements were made for all specimens and transmission electron microscopy (TEM) was used.

3. Results

TEM micrograph of the as-quenched Al_{98.5}Zr_{1.5} alloy shows fine but rather poorly defined grains with subgrains (Fig. 1a). Angular (polyhedral) structures [15] were occasionally observed but no second phases were detected indicating zirconium is all in solid solution. The alloy Al_{96.5}Zr_{3.5} showed similar microstructures, however with an increased density of angular structures. An annealing of Al_{98.5}Zr_{1.5} at 450°C for 70 min resulted in grain growth that completely eliminated the as-quenched microstructures (Fig. 1b). Coarse Al₃Zr compound particles appear along grain boundaries resulting in precipitate free zones (PFZs) and fine precipitates are formed inside grains. A similar microstructure with a denser compound distribution was obtained from alloy Al_{96.5}Zr_{3.5} after the same annealing.

Fig. 2a shows as-quenched microstructures of Al_{95.5}Zr_{1.5}B₃. Grains are finer and better defined than in Al_{98.5}Zr_{1.5}. There was some indication of ultra fine compound particles but no angular structures were observed. When annealed at 482°C for 70 min, grain size was doubled and the grain boundaries of the equiaxed grains are strongly pinned by fine precipitates (Fig. 2b). It is noted that the grain size and the precipitate size remained virtually unchanged at temperatures

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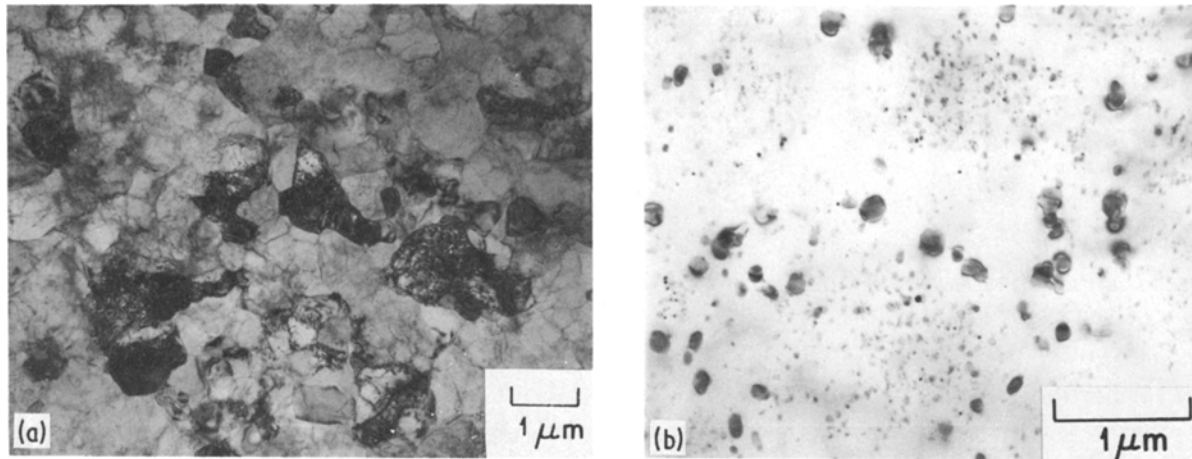


Figure 1 (a) As-quenched $\text{Al}_{98.5}\text{Zr}_{1.5}$ alloy, bright-field, (b) annealed $\text{Al}_{98.5}\text{Zr}_{1.5}$ alloy at 450°C for 70 min, bright-field.

up to 500°C . It is believed that the precipitates are ZrB_2 as will be discussed later.

Very different microstructures were observed in as-quenched $\text{Al}_{93.5}\text{Zr}_{3.5}\text{B}_3$ (Fig. 3a). Grains are less well defined and larger than in as-quenched $\text{Al}_{95.5}\text{Zr}_{1.5}\text{B}_3$ and angular structures and precipitates are observed. The electron diffraction patterns (Fig. 3b) exhibit three extra ring patterns inside the first aluminium ring pattern (indicated by an arrow). These extra rings were identified as reflections from Al_3Zr . The existence of ZrB_2 or AlB_2 was not clearly determined. When annealed at 450°C for 70 min the alloy underwent extensive microstructural changes (Fig. 3c): (a) the angular structure disappeared; (b) large, rod-shaped compounds appeared; (c) spherical precipitates similar to those in annealed $\text{Al}_{95.5}\text{Zr}_{1.5}\text{B}_3$ were formed; and (d) grains are significantly coarsened.

Isochronal annealing experiments were conducted for high zirconium-containing alloys, $\text{Al}_{93.5}\text{Zr}_{3.5}\text{B}_3$ and $\text{Al}_{90.5}\text{Zr}_{3.5}\text{B}_6$. The resulting hardnesses measured at room temperature are shown in Fig. 4 as a function of annealing temperature. It is interesting but difficult to understand why both alloys have the same hardness after quenching. However, annealing behaviour differs markedly. Alloy $\text{Al}_{93.5}\text{Zr}_{3.5}\text{B}_3$ increases in hardness slowly with annealing temperature to reach its maximum value at 200°C . A gradual hardness decrease

due to coarsening of compounds (Fig. 3c) is observed at higher temperatures. In alloy $\text{Al}_{90.5}\text{Zr}_{3.5}\text{B}_6$, the hardness remains unchanged up to 200°C . It is noted that this alloy and alloy $\text{Al}_{95.5}\text{Zr}_{1.5}\text{B}_3$ have a zirconium/boron ratio of ~ 0.5 .

Fig. 5 shows the isothermal annealing curves of alloy $\text{Al}_{90.5}\text{Zr}_{3.5}\text{B}_6$ at different annealing temperatures. It is observed that with increasing annealing temperature, the age hardening occurs faster and accordingly the time for reaching the respective maximum is reduced. The stability time of the hardening at the maximum value is also decreased with increasing temperature. It appears that the highest hardness value is achieved after 10^3 sec at 450°C .

4. Discussion

Solubility of both zirconium and boron in aluminium is close to zero at room temperature but ~ 1 at % and ~ 2 at % at 1000°C , respectively. A complete solid solution of as-quenched Al-Zr-B alloys requires both superheat beyond liquidus temperature and a very high quench rate. In the present experiments, a complete solid solution could not be achieved as evidenced by angular structures and/or some precipitates observed.

Microstructural features of Al-Zr-B alloys appear to strongly depend on the zirconium/boron ratio. At

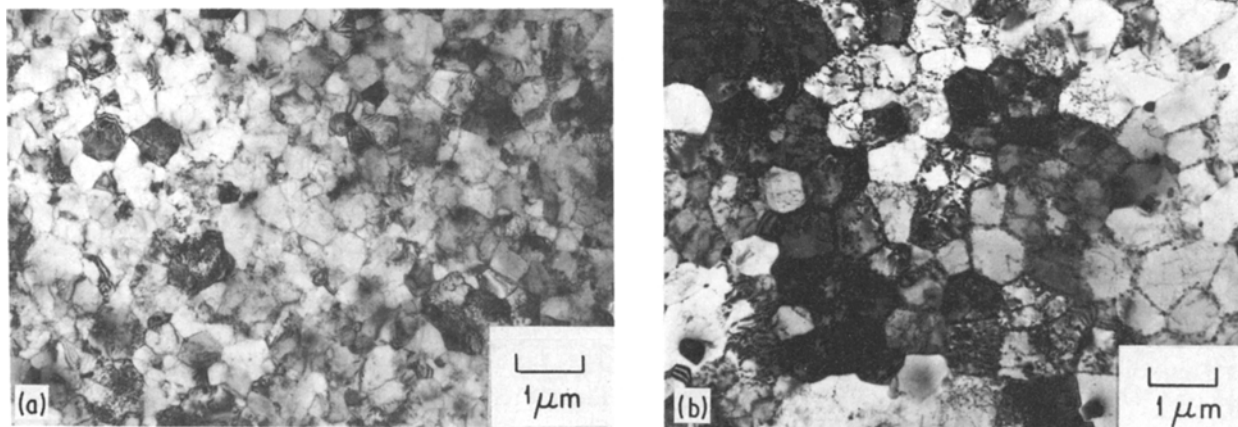


Figure 2 (a) As-quenched $\text{Al}_{95.5}\text{Zr}_{1.5}\text{B}_3$ alloy, bright-field, (b) annealed $\text{Al}_{95.5}\text{Zr}_{1.5}\text{B}_3$ at 482°C for 70 min, bright-field.

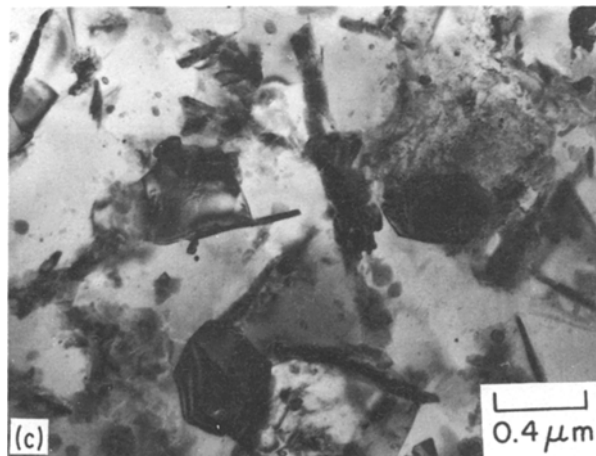
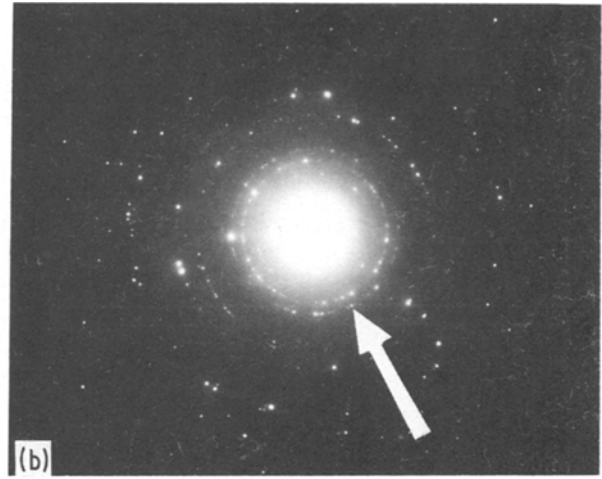
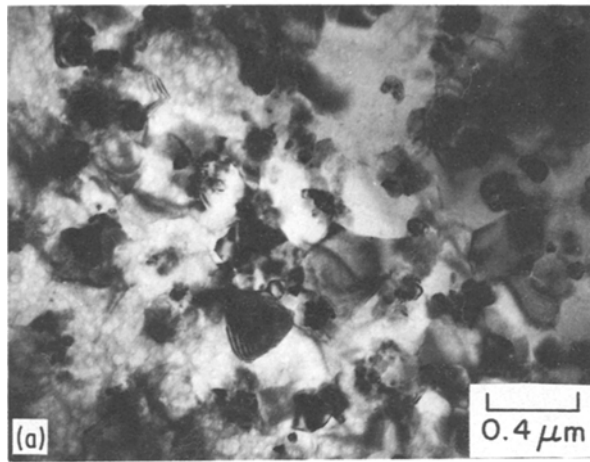


Figure 3 (a) As-quenched $\text{Al}_{93.5}\text{Zr}_{3.5}\text{B}_3$ bright-field, (b) diffraction pattern from Fig. 3a, (c) annealed $\text{Al}_{93.5}\text{Zr}_{3.5}\text{B}_3$ alloy at 450°C for 70 min, bright-field.

liquid $\rightarrow \text{TiB}_2 + \text{Al}_3\text{Ti} + \text{Al}$ in the titanium-rich corner or liquid $\rightarrow \text{TiB}_2 + \text{AlB}_2 + \text{Al}$ in the aluminium-rich corner occurs depending on the titanium/boron ratio [10]. If an analogy of the present Al–Zr–B system with the Al–Ti–B system is true, Al_2Zr and ZrB_2 compounds prevail at high zirconium/boron ratios, which is consistent with the presence of Al_3Zr in aged $\text{Al}_{93.5}\text{Zr}_{3.5}\text{B}_3$ alloys.

Acknowledgements

S. H. Whang and Y. Q. Gao would like to thank the Barnett Institute for its support. Contribution No. 175 from the Barnett Institute.

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low zirconium/boron ratios as-quenched microstructures are finer and better defined ($\text{Al}_{95.5}\text{Zr}_{1.5}\text{B}_3$, Fig. 2a) than at high ratios ($\text{Al}_{93.5}\text{Zr}_{3.5}\text{B}_3$, Fig. 3a). The same is true after annealing (Figs 2b and 3b). The slow coarsening in a low zirconium/boron ratio alloy (Fig. 2b) is due to ZrB_2 and this is reflected by the annealed curve (Fig. 4). This behaviour is similar to that of Al–Ti–B alloys where fine, coarsening resistant TiB_2 particles pin grain boundaries when the titanium/boron ratio is low [16].

It is known that in the Al–Ti–B system, either

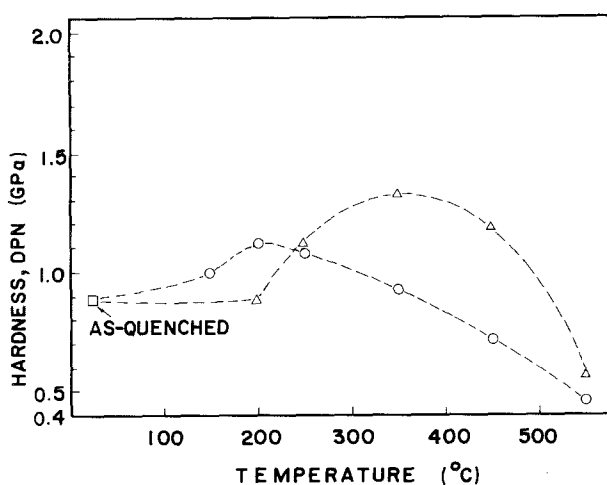


Figure 4 Microhardness of alloys (O) $\text{Al}_{93.5}\text{Zr}_{3.5}\text{B}_3$ and (Δ) $\text{Al}_{90.5}\text{Zr}_{3.5}\text{B}_6$ as a function of annealing temperature for isochromal annealing. Error $\pm 2\%$.

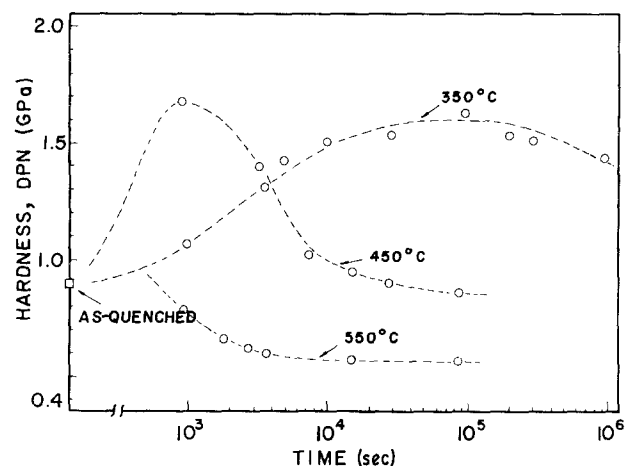


Figure 5 Microhardness of $\text{Al}_{90.5}\text{Zr}_{3.5}\text{B}_6$ alloys as a function of annealing time at 350, 450 and 550°C . Error $\pm 2\%$.

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*Received 10 September
and accepted 11 October 1985*