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Characterisation of an $Al_{93}Fe_3Cr_2Ti_2$ alloy obtained by spray forming

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ABSTRACT

$Al_{93}Fe_3Cr_2Ti_2$ is a highly promising alloy due to its capacity to form quasicrystals. In the present work bulk $Al_{93}Fe_3Cr_2Ti_2$ obtained by spray forming is microstructurally characterised. A microstructure gradient is observed, in which the external layer consists of an α-Al matrix with Al_3Ti precipitates and fine quasicrystals while the internal core presents intermetallics of the equilibrium phases $Al_{13}Cr_2 + Al_{13}Fe_4$, with intermediate stages between both areas. The hardness ranges from the 140 Hv of the external layer to the 90 Hv of the core. Spray forming can therefore produce nanoquasicrystalline $Al_{93}Fe_3Cr_2Ti_2$ which evolves towards equilibrium as the process proceeds, due to the heating produced by the deposition of successive layers.

1. Introduction

Nano-size quasicrystalline (QC) structures have been a matter of interest in recent years due to their potential for reinforcing advanced engineering alloys [1]. Icosahedral phases are hard and brittle due to the difficulty of dislocation movement in the quasiperiodic lattice without long range periodicity. However, the use of such quasicrystalline phases for the reinforcement of ductile matrices like Al alloys affords a potential improvement in mechanical properties and enhanced stability at high temperatures.

In previous studies $Al_{93}Fe_3Cr_2Ti_2$ nanoquasicrystalline (nano-QC) powders have been obtained by gas atomisation [2,3] and consolidated via warm extrusion into bars, showing high strength with good ductility at intermediate and high temperatures [4]. These good mechanical properties remain up to 450 °C and subsequently decrease with temperature. Melt-spun nano-QC ribbons have also been obtained [5]. The high strength of the alloy is achieved by a combination of solid solution, particle dispersion and grain refinement, while its stability seems to be due to the slow coarsening rate of the icosahedral phase [6].

Spray forming is an alternative casting process for near net shape billets, and although not a conventional rapid solidification (RS) process it may provide an opportunity to produce new types of alloys and bulk structures. Thus, spray-formed Al alloys containing a significant volume fraction of amorphous phases have been reported [7,8].

2. Experimental techniques

Al–3Fe–2Cr–2Ti (atomic %) alloys were spray formed using the Sandvik–Osprey plant installed at Oxford University with process conditions described elsewhere [9], obtaining billets of diameter 200 mm, height 155 mm and weight 19.2 kg. Different cross-section areas were studied by means of X-ray diffraction (XRD) using Cu Kα radiation; differential scanning calorimeter (DSC) under an argon flow at a constant rate of 20 °C/min from room temperature to 600 °C; optical microscopy (OM); scanning electron microscopy (SEM) equipped with an analysis unit (EDS); and Vickers microhardness measurements (Hv) with a load of 25 g applied for 15 s, taking the average of at least 20 indentations per sample.

3. Results and discussion

Spray forming procedure gives rise to different areas in the billet because of the different cooling rates during solidification and further thermal treatment, due to the contact with progressively deposited powder. These areas would exhibit different microstructures and properties.

A cross-section of the spray-formed billet was cut as shown in Fig. 1 to obtain representative samples of the different areas of the billet. Six areas were studied: top centre (TC), middle centre (MC), bottom centre (BC), top external (TE), middle external (ME), and bottom external (BE), studying vertical (1) and horizontal (2) sections in each case.

Fig. 2 shows the XRD patterns of the top centre (TC), middle centre (MC), and bottom centre (BC) samples, where the main peaks of the identified phases had been pointed out: α-Al, Al_3Ti, $Al_{13}Cr_2$, $Al_{13}Fe_4$ and the quasicrystal, the QC peaks overlapped with some of the $Al_{13}Cr_2$ phase. The XRD pattern of the TC sample shows signal of α-Al and Al_3Ti, as well as some peaks which could match with $Al_{13}Cr_2$ and/or QC phases. XRD patterns, or rel-

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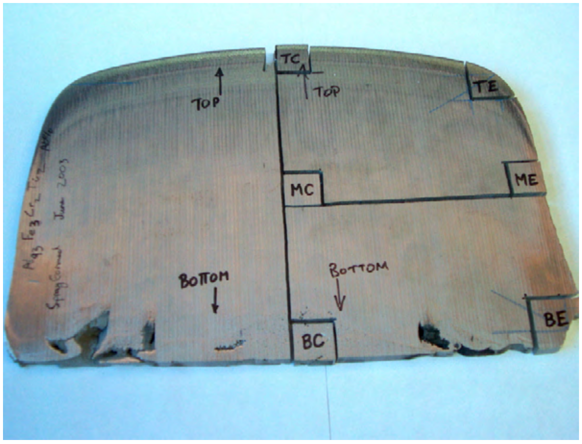

Fig. 1. Cross-section of the spray-formed $Al_{93}Fe_3Cr_2Ti_2$ billet.

ative weight distribution of phases, are similar for all the external samples (TC, TE, ME and BE), presumably undergoing similar formation conditions. The XRD pattern of the BC sample, the earliest spray formed, shows clearer signals of the equilibrium $Al_{13}Cr_2$ phase, $Al_{13}Fe_4$ and a small Al_3Ti signal. The presence of equilibrium phases suggests that powder immediately deposited above this area induce an annealing process that gives rise to the transformation of the metastable phases towards more stable ones. The MC sample presents an intermediate state with Al, Al_3Ti, $Al_{13}Cr_2$ and/or QC, and traces of $Al_{13}Fe_4$. Differences were not appreciable between vertical and horizontal sections. Therefore the XRD patterns evolve from α-Al + Al_3Ti + $Al_{13}Cr_2$ and/or QC towards α-Al + $Al_{13}Cr_2$ + $Al_{13}Fe_4$ + Al_3Ti.

The DSC traces of samples from the external group (TC in Fig. 3) reveal a wide exothermal reaction with onset at 350 °C and a released heat of 34.7 J/g. This exothermic reaction is similar to that observed in as-atomised powder of the same composition [2], and has been attributed to the QC transformation. The DSC traces of the MC and BC samples show smaller exothermic reactions starting at around the same temperature and with released heats of 5.7 and 7.5 J/g, respectively. These exothermic reactions indicate, in agreement with the XRD data, a significant amount of QC in the surface of the billet, and a lot less inside it.

Optical microscopy shows a considerable amount of porosity, with pore sizes ranging from a few microns to 15 µm. Larger pores may be attributed to solidification shrinkage, while smaller and spherical pores are due to entrapped gas. As regards the microstructure, inhomogeneous precipitation is observed. A 1% area porosity and 25–30% of intermetallic particles had been measured previously [10] (Fig. 4).

Fig. 5 presents micrographs of the three types of microstructure observed by SEM and analysed by EDS. The external samples

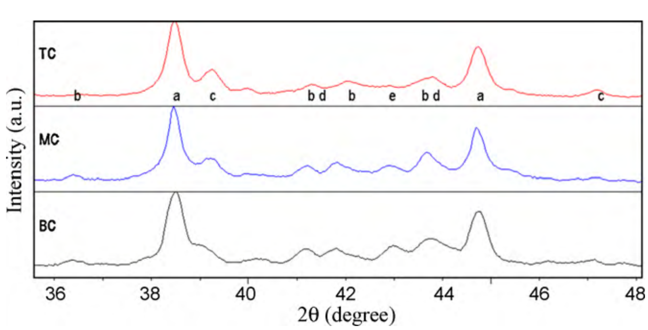

Fig. 2. XRD patterns: (a) α-Al, (b) $Al_{13}Cr_2$, (c) Al_3Ti, (d) QC, and (e) $Al_{13}Fe_4$.

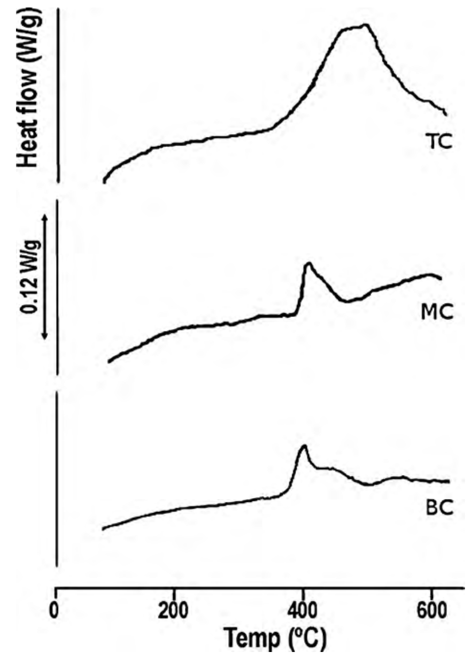

Fig. 3. Differential scanning calorimeter traces.

TC, TE, ME and BE show an inhomogeneous microstructure with zones having different precipitation grades, probably resulting from different non-remelted droplets as can be seen in Fig. 5a. The precipitates are mainly X-like Ti rich precipitates of sizes up to 5 µm and submicron globular precipitates of around 300 nm in size (Fig. 5b), which could easily be quasicrystals, because this shape is the characteristic of the QC of this alloy as has been observed in previous works [2–4]; on a grain structure of 1 µm size. The MC sample (Fig. 5c) presents an intermediate state with a high density of micrometric and submicrometric particles with X-like and needle-like precipitates. On the other hand, the BC sample (Fig. 5d) presents a comparatively low density of large Fe rich needle-like precipitates, up to 20 µm length, and irregular Cr rich precipitates of several microns in size in addition to a few small globular precipitates, which could be QC. This confirms that spray forming of the $Al_{93}Fe_3Cr_2Ti_2$ alloy gives rise to the formation of a nanoquasicrystalline structure which is retained even inside the billet, in spite of the thermal treatments it is submitted to.

Table 1 lists the microhardness of the different areas of the billet. The external areas show the greatest hardness (140 Hv), which

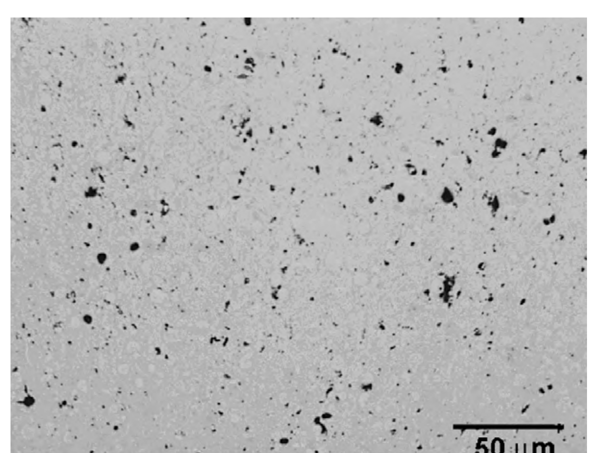

Fig. 4. Optical microscopy of a BE sample.

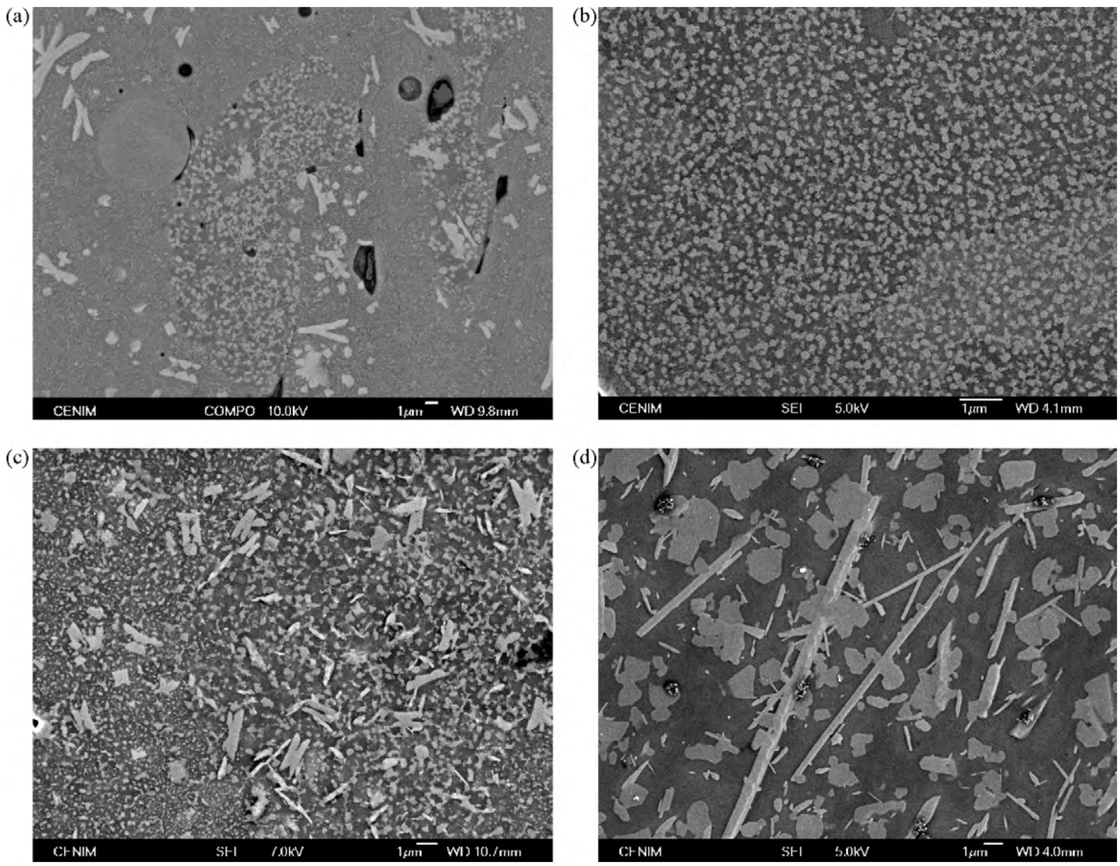

Fig. 5. SEM micrographs of (a) TC, (b) ME, (c) MC, and (d) BC samples.

Table 1
Vickers hardness.

Sample	Hv
External: TC, TE, ME, BE	140 ± 6.3
Middle centre: MC	125 ± 5.7
Bottom centre: BC	90 ± 6.6

is of the order of some extruded bars of the same composition [2]. This hardness is due to the solid solution, the fine grain size and the QC strengthening effect. The core, bottom centre, is the softest area (90 Hv) because of the decomposition of the solid solution and of the QC, and the formation of the equilibrium phases due to the stronger thermal treatment that this area undergoes. The centre area presents an intermediate hardness of 125 Hv as a consequence of the intermediate transformation state of the microstructure in this area. A previous study on extruded bars of this alloy reported a ratio of 0.2% proof stress to Vickers microhardness (Hv) of $\sigma_{0.2} = 3.18$ Hv [2], so a $\sigma_{0.2}$ close to 450 MPa can be expected in this material. The high hardness of spray-formed $Al_{93}Fe_3Cr_2Ti_2$ makes them potential candidates for coatings on wear tools.

4. Conclusions

Nanoquasicrystalline $Al_{93}Fe_3Cr_2Ti_2$ has been obtained by spray forming and is stable above 300 °C. The near 20 kg billet comprised a α-Al matrix with a high volume fraction of micron and submicron scale intermetallics, with retention of the nanoquasicrystalline phase, and high hardness at the surfaces.

As the spray forming process proceeds, the material evolves towards equilibrium due to the heating produced by the successive layers deposited, so the $Al_{93}Fe_3Cr_2Ti_2$ spray-formed billet contains three regions: external, intermediate and bottom. The external regions include non-remelted droplets with nanoquasicrystalline and Al_3Ti precipitates and present high hardness (140 Hv). The intermediate zone has a high density of Al_3Ti, $Al_{13}Cr_2$ and/or QC $Al_{13}Fe_4$ intermetallics and a hardness of 125 Hv. The bottom region, which is the first region and thus that with the strongest thermal treatment, contains large equilibrium intermetallics and is softer (90 Hv).

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References

[1] H.M. Kimura, K. Sasamori, A. Inoue, J. Mater. Res. 15 (12) (2000) 2737.
[2] I. Todd, Z. Chlup, J.G. O'Dwyer, M. Lieblich, A. García-Escorial, Mater. Sci. Eng. 375–377 (2004) 1235.
[3] A. García-Escorial, V.J. Cremashi, E. Natale, M. Lieblich, J. Alloys Compd. 434–435 (2007) 215.
[4] Z. Chlup, I. Todd, A. García-Escorial, M. Lieblich, A. Chlupová, J.G. O'Dwyer, Mater. Sci. Forum 426–432 (2003) 2417.
[5] M. Galano, F. Audebert, B. Cantor, I. Stone, Mater. Sci. Eng. 375–377 (2004) 1206.
[6] F. Audebert, F. Prima, M. Galano, M. Tomut, P.J. Warren, I.C. Stone, B. Cantor, Mater. Trans. 43 (8) (2002) 1.
[7] C.R.M. Afonso, C. Bolfarina, C.S. Kiminami, N.D. Bassim, M.J. Kaufman, M.F. Amateau, T.J. Eden, J.M. Galbraith, Scripta Mater. 44 (2001) 1625.
[8] M.L. Ted Guo, Chi Y.A. Tsao, J.C. Huang, J.S.C. Jang, Mater. Sci. Eng. A 404 (2005) 49.
[9] C. Banjongprasert, S.C. Hogg, I.G. Palmer, P.S. Grant, Macrosegregation in Novel Spray Formed Al–Li Based Alloys Proceedings of SP07, Sheffield, 2007, p. 636.
[10] C. Banjonprasert, S.C. Hogg, I.G. Plamer, N. Grennan-Heaven, I.C. Stone, P.S. Grant, Mater. Sci. Forum 561–565 (2007) 1075.