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Structure of Rapidly Solidified Al-Fe-Cr-Ce Alloy

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Abstract. An alloy containing Al – 3wt.% Cr – 3wt.% Fe – 0.8wt. % Ce, was prepared by melt spinning. Structure of obtained ribbons was observed by light, scanning and transmission electron microscopy. It was found out that the structure is very fine. Microhardness of cross sectioned ribbons was also measured. Defects in structure were determined by positron annihilation spectroscopy. The thermal stability of the alloy was observed by comparing rapidly solidified ribbons and ribbons annealed at 400°C and at 500°C for 100 h.

Introduction

Rapidly solidified (RS) aluminium alloys are promising materials for structural applications. Their main advantage is their superior strength-to-weight ratio. The best mechanical properties and thermal stability are achieved in aluminium – transition metal (TM) – rare earth metal (RE) alloy system with aluminium contents higher than 80% [1, 2]. Structure and phase composition of these alloys is strongly dependent on chemical composition and also on cooling rate during rapid solidification.

A systematic study of rapidly solidified alloys started in early 60's of the last century and the first experiments are connected with a name of P. E. Duwez. Since that time, a great variety of methods for preparing rapidly quenched alloys have been developed. Of course, some of them were more successful than the others for example because of simpler construction. At the present time, the most popular methods are: atomisation by inert gas, melt spinning, thin surface layer melting [3] and centrifugal atomization.

The rapid solidification processing involves exceptionally high rates of cooling (10^4 –10^8 K/s) during solidification from the molten state. The levels of undercooling achievable at such high cooling rates lead to significant and often potentially beneficial modifications of rapidly solidified microstructures compared with those produced under conventional conditions [4]. The rapid solidification causes an increase of the solubility of alloying elements, a refinement of the

microstructure and improves material homogeneity. The rapidly solidified materials also contain many structure defects such as dislocations, vacancies and vacancy clusters. In materials prepared under conventional conditions, these defects are usually accompanied by atmospheres of alloying elements, which enables to decrease internal stress caused by the presence of defects. The cooling rates by rapid solidification process are sufficiently high to suppress diffusion, which is a driving force for formation of large intermetallic phases and content of alloying elements in the matrix is higher than the equilibrium one. It can be expected that rapidly solidified alloy will not contain the atmospheres of alloying elements surrounding the structural defects. At elevated temperatures, diffusions rates of alloying elements increase, so it is possible that the atmospheres around defect can be formed. To prove this, the positron annihilation spectroscopy was used for rapidly solidified ribbons and ribbons annealed at 400°C for 100 h.

Experimental

An alloy containing 93.08 wt.% Al – 3.17 wt.% Cr – 2.92 wt.% Fe – 0.83 wt. % Ce, denoted as AlCr3Fe3Ce1, was prepared by melt spinning with circumferential speed of cooling wheel of 20 m/s. Chemical composition was determined by x-ray fluorescence spectroscopy (XRF) using spectrometer ARL 9400 XP. The ribbons were observed at cross section by Olympus PME3 light microscope. Vickers hardness HV 0.02 was also determined on the cross sectioned ribbons. Transmission electron microscopy (TEM) samples were prepared by grinding the 3mm disc to the thickness of 50 μm. Consequently, they were dimpled by Gatan Dimple Grinder, Model 656 to the final dimple thickness of 10 μm and precision ion polished by Gatan PIPS, the Model 691. TEM samples were examined by using a transmission electron microscope Jeol 3010 (accelerating voltage 300 kV). The conventional x-ray diffraction was measured on the wheel side of the ribbon by PAN analytical X'Pert PRO + High Score Plus with Cu anode. The Topas3 program was utilized for Rietveld structure refinement. High energy x-ray diffraction measurements were performed at BW5 beamline located at the DORIS III positron storage ring in DESY Hamburg. Monochromatic synchrotron radiation with wavelength of λ=0.124 Å was used for measurement. Positron annihilation spectroscopy (PAS) involves several experimental techniques: (i) positron lifetime (LT) spectroscopy makes it possible to identify the type of defects and to determine their concentrations; (ii) coincidence measurements of Doppler broadening (CDB) is a unique method which brings information about the local chemical environment of defects. The detailed description is given elsewhere [5, 6]. The time resolution of the digital LT spectrometer was 150 ps (FWHM, ^{22}Na). At least 10^7 annihilation events were accumulated in each LT spectrum. At least 10^8 events were collected in each CDB spectrum. The relative changes of Doppler profiles were followed as ratio curves of the Doppler profile normalized counts to those of the well annealed pure Al (99.9999%) reference profile.

Results and Discussion

Structure of rapidly solidified AlCr3Fe3Ce1 alloy was very fine, as illustrated on the cross sectioned in Fig. 1. The value of ribbons thickness was about 50μm and the ribbon exhibited structural gradient caused by decreasing cooling rates with increasing distance from cooling wheel. The wheel side of the ribbon is placed in the down part of Fig. 1. The alloy was formed by fcc-Al grains and intermetallic phases surrounding the grains, as shown in Fig. 2.

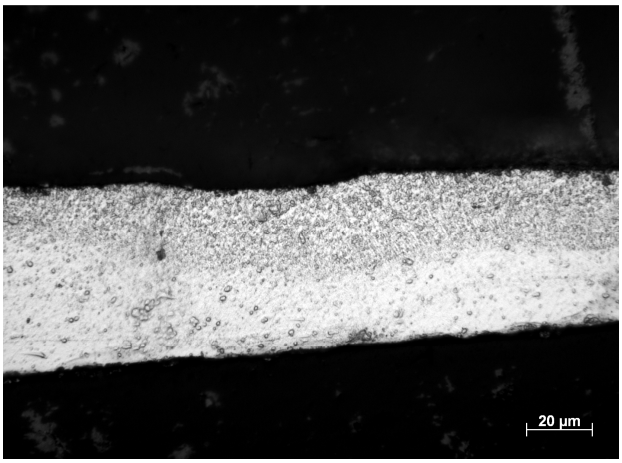

Fig. 1. Cross section of RS AlCr3Fe3Ce1 alloy ribbon (LM)

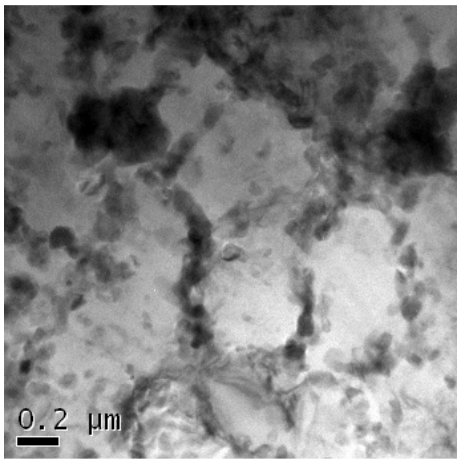

Fig. 2. TEM micrograph of RS AlCr3Fe3Ce1 alloy

The structure was not changed after annealing at 400°C for 100 h, as documented in Fig. 3. On the other hand, an annealing at 500°C for 100 h lead to significant microstructural changes, such as grain coarsening and occurrence of new phase, as shown in Fig. 5. The comparison of grain sizes of RS and annealed materials is given in Tab. 1.

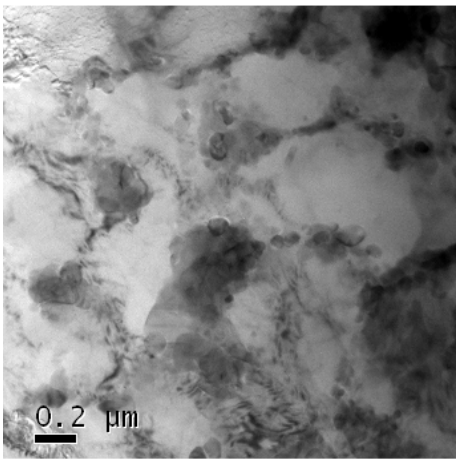

Fig. 3. TEM micrograph of AlCr3Fe3Ce1 alloy annealed at 400°C for 100 h

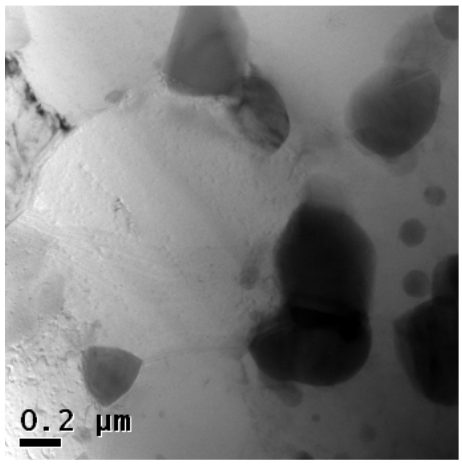

Fig. 4. TEM micrograph of AlCr3Fe3Ce1 alloy annealed at 500°C for 100 h

Decrease of hardness value was also observed after long term annealing at 500°C, as can be seen in Tab. 1. While the hardness of RS alloy and alloy annealed at 400°C are approximately the same, the value for alloy annealed at 500°C is significantly lower. Grain size was determined by two ways – by image analysis and by Rietveld refinement of XRD patterns, which allows determining the size of coherently diffracting domains. This is the reason for difference in absolute values obtained by different methods. However, the trend in grain size evolution was observed by both methods. The grain size for RS alloy and annealed at 400°C was the same within the measurement accuracy, the grain size of alloy annealed at 500°C was approximately two-times higher.

Tab.1. Hardness, average grain size determined by image analysis and by Rietveld refinement from XRD patterns for RS AlCr3Fe3Ce1 alloy and alloys annealed at 400°C and 500°C for 100 h

Alloy	Hardness HV0.02	Grain size by image analysis / nm	Grain size by XRD / nm
RS	116 ± 4	294 ± 6	165 ± 4
annealed 400°C/100h	110 ± 3	313 ± 6	148 ± 3
annealed 500°C/100h	71 ± 1	509 ± 19	211 ± 5

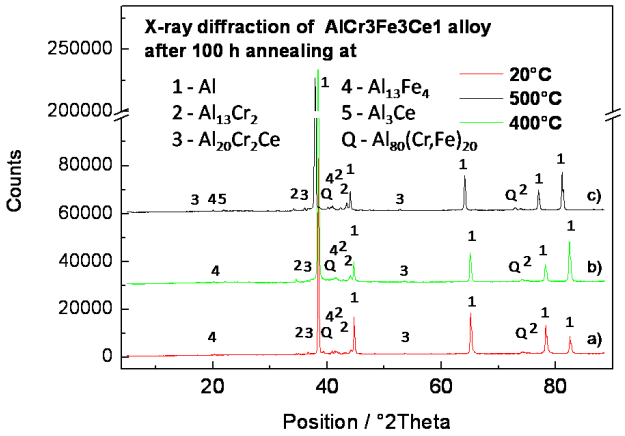

Fig. 5. XRD patterns of AlCr3Fe3Ce1 alloy a) RS, b) annealed 400°C/100h, c) annealed 500°C/100h

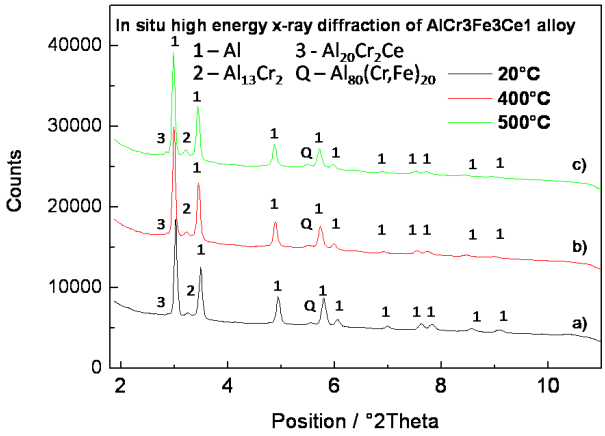

Fig. 6. High energy XRD patterns of AlCr3Fe3Ce1 alloy a) at 20°C, b) at 400°C, c) at 500°C

The RS alloy composed of fcc – Al, $Al_{13}Cr_2$ and $Al_{20}CeCr_2$ intermetallic phases and small amount of $Al_{80}(Cr,Fe)_{20}$ quasicrystalline phase. After annealing at 500°C for 100 h an Al_3Ce phase arisen. This phase was not observed during in-situ high energy diffraction at 500°C, see Fig. 6. The process of new phase formation is strongly dependent on diffusion rate of alloying elements and so the new phase can be detected after long term annealing and not directly after heating of the alloy.

The main structure defects detected in RS AlCr3Fe3Ce1 alloy by PAS were dislocations. They were not distributed homogenously in material, as was proven by LT, and they formed dislocation walls with dislocation density of 4 x10^{14} m^{-2}, while the average dislocation density was 9 x 10^{13} m^{-2}. For the PAS experiments, pseudo- bulk sample was prepared formed by several ribbons. In this case, the dislocation walls corresponded to the wheel sides of ribbons, that were cooled at highest quenching rates and so they contain more structure deformation. The chemical composition in vicinity of dislocations was the same as matrix composition, as proven by CDB. Results obtained for ribbons annealed at 400°C for 100 h were similar to results of RS ribbons. In further research, the ribbons annealed at 500°C for 100 h will by studied by PAS.

Conclusion

The rapidly solidified ribbons of AlCr3Fe3Ce1 alloy were formed by fine- grained fcc-Al, intermetallic phases and small amount of quasicrystalline phase. The alloy exhibit excellent thermal stability at 400°C. Grain coarsening and formation of new phase was observed at 500°C.

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References

[1] A. Inoue, et al.,: NanoStructured Materials, 11 (1999)221

[2] K. Saksl, et al., Journal of Applied Physics 97, 113507 (2005)

[3] B. Bártová, et al.,: Journal of Alloys and Compounds, 387 (2005), 193-200

[4] Z. Zhang, et al.,:, Journal of Crystal Growth 281 (2005) 646-653

[5] F. Bečvář, et al.,: Nucl. Instr. Meth. A 539 (2005) 372

[6] F. Bečvář, et al.,: *Acta Physica Polonica A* **113** (2008) 1279