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Rapidly solidified Al-Mo and Al-Mn ribbons: microstructure and mechanical properties of extruded profiles

M. Čavojský[1]*, P. Švec Sr.[2], D. Janičkovič[2], Ľ. Orovčík[1,3], F. Simančík[1]

[1]*Institute of Materials and Machine Mechanics, Slovak Academy of Sciences,*
Račianska 75, 831 02 Bratislava, Slovak Republic
[2]*Institute of Physics, Slovak Academy of Sciences, Dúbravská cesta 9, 841 00 Bratislava, Slovak Republic*
[3]*Faculty of Materials Science and Technology STU in Trnava, STU Bratislava,*
Paulínska 16, 917 24 Trnava, Slovak Republic

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Abstract

Two alloys of composition Al-Mo(3; 5) at.% and Al-Mn(3; 5) at.% were studied in the form of compacted cuts of rapid solidification ribbons. The structure of samples was composed of fcc α-Al solid solution oversaturated with Mo and Mn, intermetallic $Al_{12}Mo$ and Al_6Mn phases, all in ultrafine submicron grain size. The kinetics of structural changes and their effect on mechanical properties were described as a function of annealing temperature and time. The discrete RS particles (chopped ribbons) were compacted into simple structural profiles using conventional and relatively inexpensive direct extrusion method. All compacted profiles exhibited similar structure as precursor materials, incl. even grain size. Almost theoretical density with no identified porosity and gas entrapment was achieved. The extruded profiles were extremely thermally stable; no structural changes were detected even after annealing at 300 °C for 24 h. The best mechanical properties were obtained for compacted RS AlMo5 ribbons: their UTS at room temperature exceeded 385 MPa at 5 % elongation to fracture. UTS at 300 °C/24 h regularly exceeded 375 MPa what is 5 times higher than UTS of conventionally used Al alloys. Young's modulus (E) of extruded compact at RT was 90 GPa what means an increase of more than 25 % in E/ρ compared with standard Al.

Key words: aluminium, mechanical properties, melt-spinning, rapid solidification, thermal stability

1. Introduction

Aluminium (Al) alloys are widely used in the transportation industry due to their high specific strength. High strength Al alloys based on precipitation hardening (2xxx and 7xxx groups) possess strength up to ~ 700 MPa. However, these alloys show a pronounced loss of their strength at relatively low temperatures (~ 150 °C) due to over ageing effects from the high diffusivity of the main strengthening elements (Zn, Mg, and Cu) in Al. This loss limits the application of high strength Al alloys for the elevated temperature goods (e.g., engine parts as pistons, liners, etc.). The thermal stability of Al alloys can be improved by introducing alloying elements with low diffusivity in Al, such as Ni, Cr, Mn, Mo and Fe transition metals (TM) [1–3]. However, the very limited solubility of TM in Al restricts its concentration in Al alloys. Thus, the serviceable temperature limit of the high strength 2024, 2618, and 2650 alloys, the reference thermally stable Al-based alloys used for combustion engine pistons, is still below 200 °C.

The rapid solidification (RS) from the liquid state yields a supersaturation of solid solutions with alloying TM elements. Furthermore, RS results in favourable fine metastable (quasi)crystalline phases, profound structural refinement and even formation of amorphous phases. Those features ensure the high strength of RS Al alloys accompanied by enhanced thermal stability. However, the associated heat flow

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*Corresponding author: tel.: +421/259309414; fax: +421/244253301; e-mail address: miroslav.cavojsky@savba.sk

Table 1. The chemical composition of the melt-spun ribbons (wt.%)

Composition of ribbons	elements							
	Al	Mo	Mn	Si	Fe	Mg	Cu	P
AlMn3 (at.%)	rest	0.0	4.65	0.06	0.06	0.02	0.005	0.001
AlMn5 (at.%)	rest	0.0	8.55	0.2	0.02	0.04	0.006	0.001
AlMo3 (at.%)	rest	9.63	0.02	0.04	0.02	0.02	0.005	0.001
AlMo5 (at.%)	rest	15.5	0.02	0.05	0.02	0.04	0.006	0.001

limits at least one dimension of the RS structure. Thus, the consolidation of discrete RS particles via powder metallurgy (PM) is required to form bulk products. The consolidation is basically circumscribed to the compaction route based on introducing shear deformation (mostly extrusion) at moderate temperatures (~ 400 ℃) to maintain the RS microstructures and establish good metallurgical bonding between particles. However, the RS structures generally have poor workability at low extrusion temperatures as a result of their high strength and low ductility [4], which leads to improper consolidation or to a loss of mechanical properties (i.e., desired microstructures) at high temperatures of compaction. Thus, the successful consolidation of high-strength RS Al-based alloys is the most challenging technological task in the field of Al powder metallurgy.

Additional alloying with other low diffusion elements (X = Fe, Ti, Mo, Mn) brings up synergistic effects in stabilising and precipitation hardening by the presence of fine stable AlX and AlCrX precipitates. The RS Al-Cr-Fe alloys have been studied for more than three decades [5–8], which has established their high temperature mechanical strength that accompanies their excellent thermal stability. However, to our knowledge, there are no substantial applications of RS Al-Cr alloys [9]. A positive feature of the PM process is that it involves rapid solidification of the melt, which is directly related to the structural refining of the PM alloys. The subsequent ultra-high pressure compaction of rapidly solidified powders ensures good diffusion bonding between particles. Alternatives to this compaction process could be hot extrusion or die forging. Through the current work, PM technology is shown to be a viable technology for processing Al-based alloys with high contents of transition metals [8]. The thermal stability and creep tests reveal that the PM alloys outperform (by more than a factor of three in the creep test) the casting alloy, which is commonly considered to be thermally stable [10, 11]. In this study, an industrial feasibility study was performed for a large-scale production of Al-Mo and Al-Mn alloy prepared in the form of melt spun ribbons and subsequent consolidation of discrete RS particles by extrusion.

2. Experimental

The reference material was prepared in the form of melt-spun ribbons produced by planar flow casting, and cast at a temperature of 1290 ℃ on to a Cu cooler rotating at 43 $\mathrm{m\,s^{-1}}$. The width of as-spun ribbons was ~ 10 mm with an average thickness of 25 μm. As-spun ribbons were fragmented using a special cryo-chopping approach that maintained their plasticity. Only the size fraction below 500 μm was used. Loose chopped ribbons were heated up to an extrusion temperature of 330–400 ℃ for 10 min under air prior to direct extrusion (DE). DE was performed at an average ram speed of ~ 1 $\mathrm{mm\,s^{-1}}$ using an extrusion ratio of $R = 11:1$ into the rods with diameter of 6 mm. Density of cold isostatic pressing (CIP) green bodies was ~ 81 % of the theoretical density (THD) [12, 13]. Extruded profile was slowly cooled down at air environment to room temperature. The composition of the melt-spun ribbons is shown in Table 1.

In order to study thermal stability of feedstock materials as well as final profiles, annealing at 200, 300, 350, 400 and 450 ℃ for 24 h was carried out. The density of the profiles was measured by Archimedes method. The crystallisation behaviour, thermal stability and microstructural characterisation were studied using TEM (Jeol JEM 200CX), FEG-SEM EDS WDS (Jeol 7600F), XRD (Philips X'Pert) and DSC (Perkin-Elmer DSC7). The mechanical properties in tension were measured on tensile bars with a gauge of ø 5–30 mm using a ZWICK testing machine at a cross ram speed of $6 \times 10^{-4}\ \mathrm{min^{-1}}$. HV hardness measurements were carried out using a 0.049 N load and a 5 s dwell time. Each specimen was machined parallel to the extrusion direction. The elastic modulus was measured by DMA (dynamic mechanical analysis) on TA Q800 machine, using 5 mm × 2.5 mm × 55 mm bars and the three point bending method.

3. Results and discussion

Figure 1a shows the longitudinal cross-section of an as-extruded AlMn5 material, which shows a well compacted structure with a very small amount of voids and pores. No blistering was observed in either

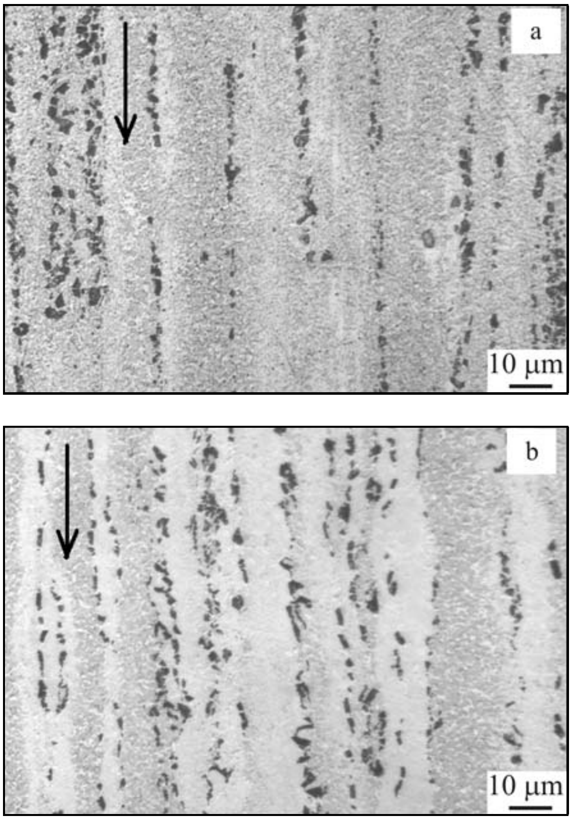

Fig. 1. Light micrograph of extruded ribbons in longitudinal cross-section (the arrow indicates extrusion direction): AlMn5 (a) and AlMo5 (b) compacts.

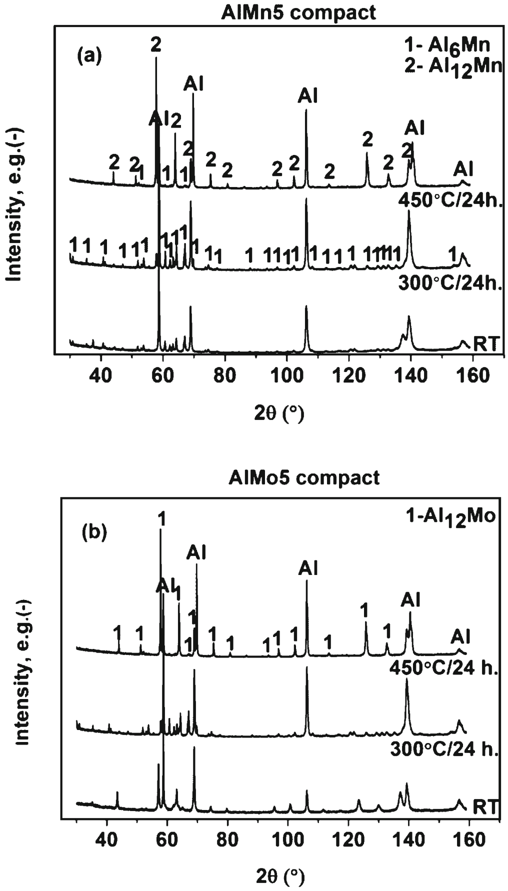

Fig. 2. XRD patterns of as-extruded alloys (AlMn5 (a) and AlMo5 (b)), room temperature and after 24 h annealing at 300 and 450 ℃.

the as-extruded state or after any of the performed annealings. The typical textured microstructure of the ribbons particles was severely elongated and arrayed in the extrusion direction. Relatively large intermetallic phase regions (dark contrast phase) embedded within the Al matrix (light contrast phase) in some elongated grains could be resolved even by LM, which agrees with other work [14]. Smaller ribbons particles cooled down at higher cooling rates exhibited a more homogeneous featureless microstructure, whereas this microstructure was also retained after extrusion (dark contrast strips). Direct extrusion yielded sound compacts with densities > 98 % of theoretical density. Light microscopy of extruded AlMo5 compacts (Fig. 1b) revealed well compacted microstructures of ribbons arrayed into the extrusion direction.

The XRD results show that microstructure for the compacts of as-spun ribbons is very similar (Fig. 2a,b). The XRD spectra confirmed the presence of following phases: α-Al, crystalline $Al_{12}Mo$ and Al_6Mn ($Al_{12}Mn$). The XRD of annealed compact confirmed the excellent thermal stability with no major structural changes determined after 24 h annealing up to 300 ℃ (Fig. 2). Above this temperature, significant change in diffraction pattern presented formation of the $Al_{12}Mn$ phase instead of Al_6Mn phase. RTG analysis confirmed that there was no difference between the microstructure and phase composition of ribbon and extruded part.

The SEM characterisation of the as-extruded compacts revealed a microstructure formed by interconnected Mn, Mo rich phase filled with Al matrix phase (Fig. 3a,c). Annealing of compacts at 450 ℃ for 24 h caused coarsening of the Mn-rich phase (Fig. 3b).

In the case of manganese system a significant thickening of the present phase could be observed at 450 ℃ compared to the extruded state. At this temperature conversion of intermetallic phase Al_6Mn into $Al_{12}Mn$ was observed by X-ray diffraction. These changes had a profound effect on the mechanical properties. It was not possible to measure mechanical properties at this temperature. The particle size of the precipitates was changed from the original 500 nm (approximately) to 5–6 microns. At the molybdenum system, the heterogeneity of the structure was flattened and a slight increase of precipitates was observed due to heat treatment at elevated temperatures (Fig. 3d). This had a positive influence on the mechanical prop-

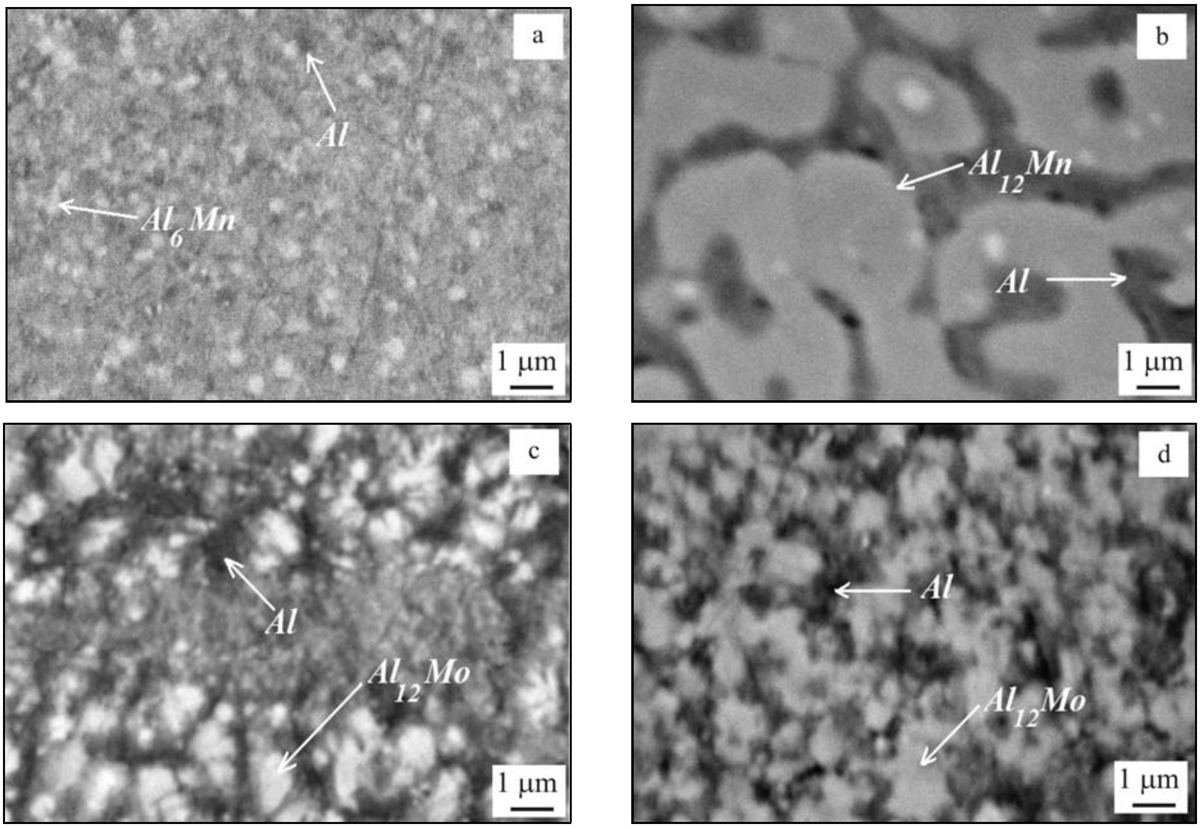

Fig. 3. SEM images of the etched as-extruded ribbons AlMn5 (a) and AlMo5 (c) and annealed at 450 ℃ for 24 h AlMn5 (b) and AlMo5 (d).

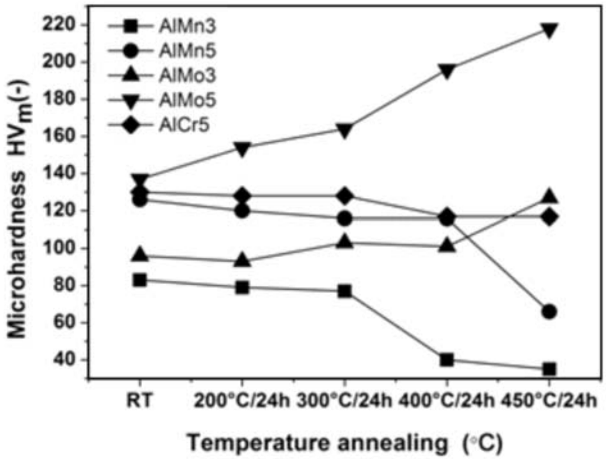

Fig. 4. HV microhardness of ribbon compacts in as-extruded state and after 24 h annealing at different temperatures [9, 15].

erties, which were improving with increasing temperature.

The long-term structural stability of compacts at 300 ℃ was indirectly measured by microhardness measurements (Fig. 4). Only minor changes in the measured HV were observed, even after prolonged exposures (24 h). The thermal stability limit after 24 h exposure at a particular annealing temperature was found to lie between 300 and 350 ℃ for AlMn compacts. There was a sharp decline in HV for this annealing temperature. In case of AlMo compacted material manufactured from ribbons, moderate increase of HV values was observed even at temperature below 450 ℃.

We found out that the as-extruded ribbon compacts AlMo showed a room temperature ultimate tensile strength 375 MPa and yield strength 260 MPa accompanied by a rather good ductility of 5 % (Table 2). The tensile properties (yield strength and Young‘s modulus) of compacts were improved after annealing at 450 ℃ for 24 h due to slight coarsening of the $Al_{12}Mo$ phase and the depletion of the Mo solid solution. Annealing at 300 ℃ as well as at 450 ℃ for 24 h affected high temperature properties of all compacts only slightly. DMA analysis proved high value of elastic Young‘s modulus $E = 88$ GPa. By flattening of structure heterogeneity due to temperature AlMo system extruded parts became stiffer thus increasing also the microhardness. On the contrary, AlMn system lost strength characteristics due to large thickening of precipitates within the structure. For comparison, also AlCr5 system is shown in Fig. 4. AlCr5 system was structurally stable up to the annealing temperature

Table 2. Tensile tests results of industrially extruded ribbons compacts performed at room temperature in the as-extruded state and after 24 h annealing at 300 and 450 °C. Young's modulus was determined by DMA. A_{10} is percentage elongation of a gauge length of 10 mm

Sample	as-extruded				300 °C/24 h				450 °C/24 h			
	YS (MPa)	UTS (MPa)	A_{10} (%)	E (GPa)	YS (MPa)	UTS (MPa)	A_{10} (%)	E (GPa)	YS (MPa)	UTS (MPa)	A_{10} (%)	E (GPa)
AlMn3	270	300	1.2	–	255	275	1.1	–	130	165	0.6	–
AlMn5	370	405	1.7	80	360	400	0.7	80	–	55	–	82
AlMo3	245	337	7.7	–	220	310	9.2	–	220	312	7.6	–
AlMo5	260	375	4.2	88	260	385	5.1	92	290	342	0.4	97

of 450 °C, which was confirmed by the measurement of the same mechanical and structural properties in [15], where no change in the structure was observed comparing to as-prepared state.

We have further found, for the extruded ribbon AlMn compacts at room temperature, an ultimate tensile strength of 405 MPa and 370 MPa yield strength, accompanied by a relatively low elongation of 1.7 % (Table 2). Compacts tensile properties are deteriorated rapidly after annealing at 450 °C for 24 h, which has been linked to the conversion of phase Al_6Mn to $Al_{12}Mn$ phase and depletion of Mn solid solution. Annealing at 300 °C, and then at 450 °C for 24 h affected the compacts properties. DMA analysis showed small values of elastic Young's modulus $E =$ 80 GPa at room temperature. Summarising, the influence of annealing temperature had a positive effect in the case of molybdenum systems, where even at a temperature of 450 °C, the yield strength slightly increased in contrast to the manganese system. At this temperature manganese system had lost all properties due to rapid thickening of present phase.

4. Conclusions

The possibility of preparation of bulk extruded profiles from the rapidly solidified ribbons AlMo and AlMn 3.5 at.% alloys was examined. "Blocky" microstructure of sound extruded compacts consisted of saturated α-Al phase with presence of nanoscale crystalline phases at room temperature and microscale after annealing at 450 °C/24 h. The extruded compacts exhibited excellent long term thermal stability up to 300 °C and high mechanical strength at elevated temperatures. Found features predetermine this material for service at elevated temperatures, with superior performance to conventional Al alloy. Commercially used alloys for pistons (e.g., A2618) usually lost the strength properties after reaching of 200 °C. Furthermore, good formability along with long-term structural stability of RS feedstock material at the used extrusion temperature enable consolidation of as-atomised powders at low extrusion pressures. Our previous investigations showed that replacing RS melt-spun ribbons with conventional atomized powders gives profiles with comparable features [15]. This makes potential for up-scaling of presented procedure feasible.

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