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CONSOLIDATION OF RAPIDLY SOLIDIFIED Al-BASED PARTICLES USING EQUAL CHANNEL ANGULAR PRESSING (ECAP)

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Abstract. Consolidation of rapidly solidified (RS) particles in particular chopped Al94Fe2V4 melt-spun ribbons (MSR) and ultra-fine Al 99.7% powders (d_{50}=1.3 μm) was performed in order to obtain bulk profiles for structural applications requiring high strength and thermal stability at elevated temperatures above 200 °C accompanied with sufficient ductility and toughness. Equal Channel Angular Pressing (ECAP) method was investigated as an alternative to conventionally used compaction via hot direct extrusion (DE). The experiments have shown, that ECAP enables introduction of sufficient shear deformation necessary for establishing good metallurgical bonds between particles at significantly lower compaction pressures than DE performed at the same temperatures. This allows compaction of Al-based particles at lower temperatures and thus maintaining their desired RS structure. Satisfactory compaction of both types of RS particles was attained already after one ECAP pass. ECAPed compacts resulted in higher microhardness and density than in a case of their extruded counterparts. Obtained properties can be still further enhanced by multiple ECAP passes.

1. INTRODUCTION

The extremely high tensile strengths exceeding 1 GPa accompanied with good ductility and thermal stability are expected from rapidly solidified (RS) Al-based alloys that microstructures consist of amorphous, nanocrystalline and quasicrystalline phases [1]. However, due to limited heat flow during rapid quenching, such fine or aperiodic phases can be obtained only in thin ribbons or fine powder particles. Since the practical application of discrete particles is limited, their synthesis into bulk materials is inevitable, whereas sufficient shear deformation is required to break surface oxides and assure sound metallic bonds. For this purpose hot extrusion is frequently used. However, the resistance against deformation of high strength materials induces extreme extrusion pressures at moderate temperatures often overtaking the limits of conventional tools [2,3]. In case of ultra-fine powders the deformation resistance is further enhanced due to high specific surface and hence high content of hardly deformable oxide layers. However, the reduction of deformation resistance by temperature increase is often not possible, especially in case of RS alloys because of potential ultimate destruction of they unique microstructure. Therefore Equal Channel Angular Pressing (ECAP), (theoretically) introducing only shear stresses into deformed material, was explored for compaction of RS particles as an alternative to conventionally used hot direct extrusion (DE), with an aim to reduce the level of redundant normal stresses and thus extraordinary loading of tool. The decrease of temperature for satisfactory compaction was expected as well.

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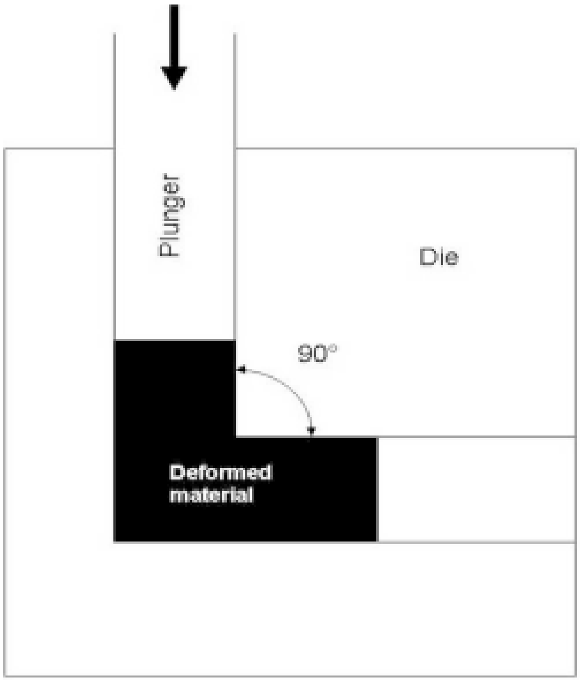

Fig. 1. Schematic illustration of ECAP die.

Table 1. Chemical composition of Al 99.7% powder in wt.%.

Al	99.82
Si	0.0533
Fe	0.1071
Cu	0.0007
Mn	<0.001
Mg	<0.005
Zn	<0.005
Ni	0.003
O_2	2.05
Cr	<0.005
Pb	<0.002
Sn	<0.005
Ti	0.0036
V	0.0059
Zr	0.0088

2. EXPERIMENTAL

The master alloy with a nominal composition of $Al_{94}Fe_2V_4$ (at.%) was prepared in vacuum induction furnace from pure elements. Rapidly solidified ribbons with a cross section of 0,02 mm x 10 mm were produced by planar flow casting (quenching rate ~10^6 °C s^{-1}). As-received ribbons were cryomilled and sieved into 63-125 µm particle size fraction. Ultrafine Al powder (x_{50}=1.31 µm, x_{10}=0.66 µm, x_{90}=2.51 µm from Helos analyse) of technical purity 99.7% (see chemical composition in Table 1) was prepared by gas atomization (N_2 atmosphere). Both particulate RS materials were first pre-compacted via cold isostatic pressing CIP at 200 MPa (1 µm Al powder) and 1 GPa ($Al_{94}Fe_2V_4$ MSR), respectively.

Some of pre-compacted RS particles were hot extruded using flat face die with extrusion ratio (ER) 11:1 or 4:1 into round rods with diameter of 6 and 10 mm respectively.

The die for alternative ECAP – compaction is schematically illustrated in Fig. 1). It consists of two rectangular channels 12 x 12 mm intersecting in 90° with sharp outer corner. The pre-compacted RS materials were machined from CIPed green bodies into cylinders ø10 x 70 mm and placed into Cu containers with outer dimensions of 12x12x90 mm, that were utilized in order to reduce mutual friction between particles and die wall. For comparison also multiple ECAP passes on the same sample were performed according to so-called "Bc route" when sample is rotated by 90° clockwise after each pass.

Measurements of density were performed via Archimedes method. Mechanical properties were evaluated in terms of HV microhardness using 10 p loading. The microstructure was characterized by light and transmission electron microscopy (TEM) using the JEOL JEM 100 C electron microscope operated at 100 kV. TEM samples were thinned electrolytically in a solution of 10% perchloric acid, 10% ethyleneglycol and 80% ethanol at – 50 °C.

3. RESULTS AND DISCUSSION

3.1. Investigation of experimental materials

Fig. 2a shows TEM micrograph of supplied 1 µm Al 99.7% powder. The powder monocrystalline particles were of spherical shape where no or only few dislocations were observed in as received powder. As no distinctive dislocations were observed in as received powder, sufficient capability for plastic deformation was expected. Exact chemical composition is summarized in Table. 1.

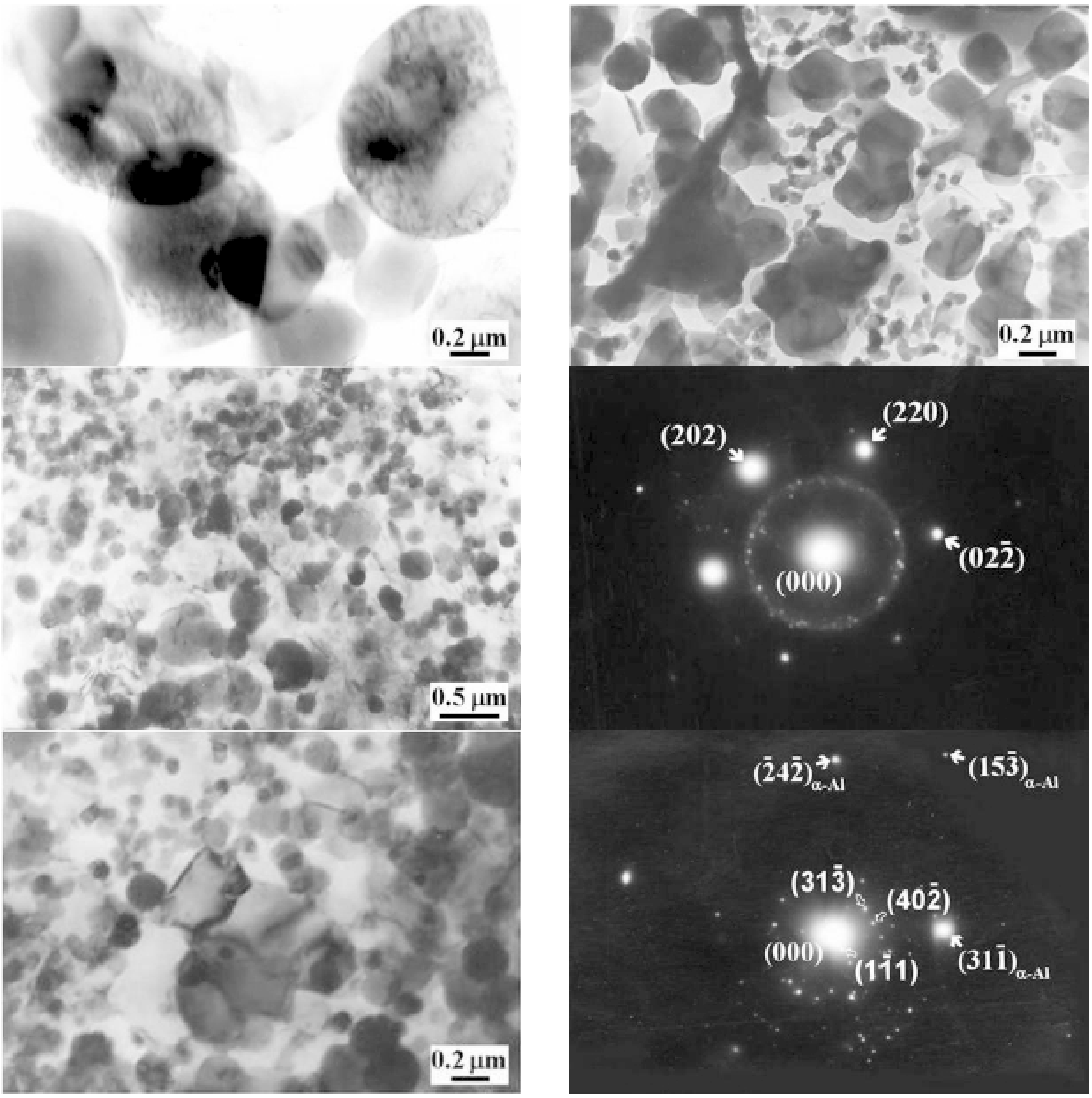

Fig. 2. TEM micrographs of 1 μm Al 99,7% powder (a), $Al_{94}Fe_2V_4$ melt-spun ribbon in as-received state (b), after annealing at 450 °C (c) and at 500 °C for 30 minutes (d).

TEM micrograph of $Al_{94}Fe_2V_4$ melt-spun ribbon in as-received state is shown in Fig. 2b. Microstructure is predominantly formed by α-Al grains and randomly oriented spherical icosahedral particles with diameters mostly not exceeding 100 nm. Moreover small amount of fcc $Al_{10}V$ intermetallic phase and amorphous phase were also present. The microstructural heterogeneity of MSR was presumably caused by cooling rate gradient within thickness of the ribbon since it varies in the range ~0-20 μm. Intermetallics were found predominantly in regions where cooling rate was not high enough to suppress crystallization [4,5].

Figs. 2c and 2d show microstructure of as-annealed MSR. Annealing at elevated temperatures led to full devitrification of amorphous phase (above 250 °C) and transformation of metastable icosahedral phases to stable intermetallic phase

Table 2. Breakthrough pressures, densities and microhardness obtained during consolidation of 1 μm Al powder via equal channel angular pressing (ECAP) and direct extrusion (DE) at various temperatures.

T [°C]	200	250	300	350	400	450	500
pressure ECAP[MPa]	800	454	358	215	-	-	-
density ECAP [g cm^{-3}]	2.65	2.66	2.66	2.67	-	-	-
HV ECAP	102.6	100.1	95.2	92.3			
pressure DE [MPa]	-	-	-	1376	1118	986	797
density DE [g cm^{-3}]	-	-	-	2.66	2.67	2.66	2.67
HV DE				102.2	96.1	87.3	85.9

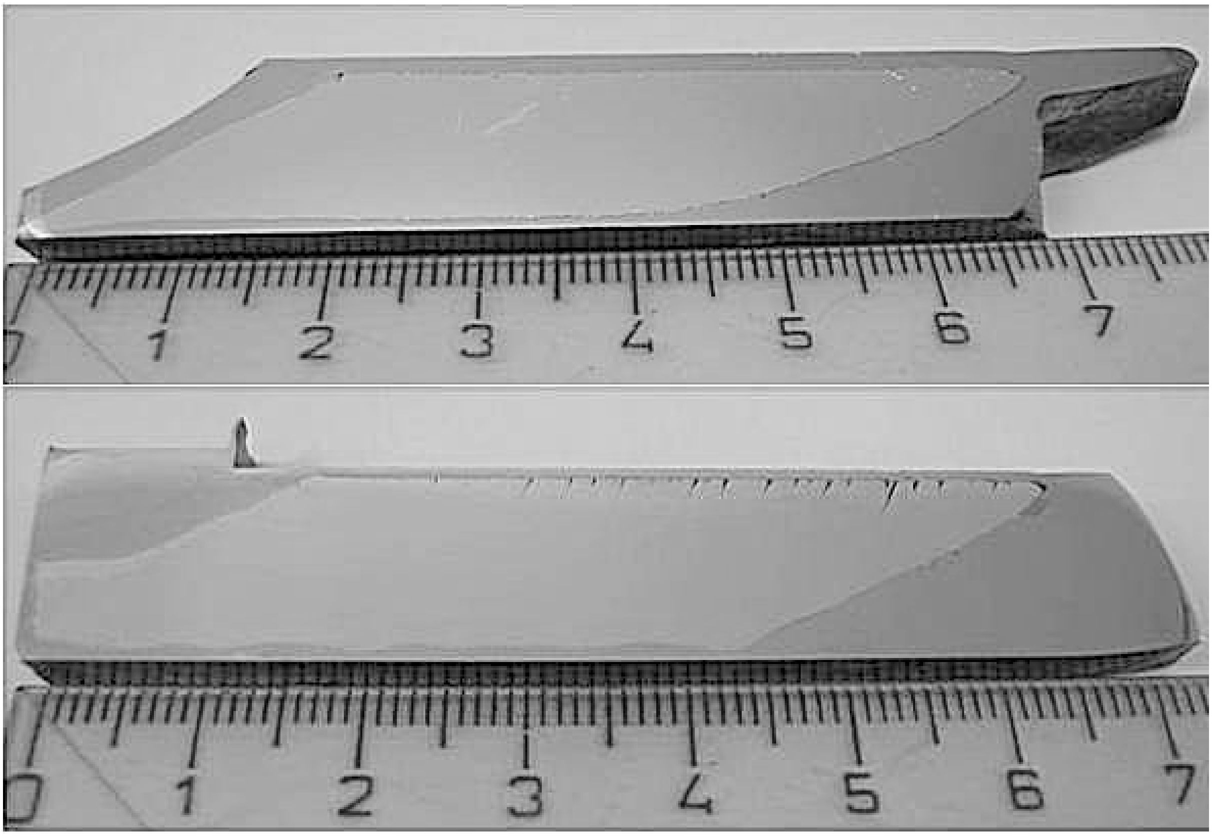

Fig. 3. ECAP compacts of 1 μm Al 99.7% powder prepared at non optimized (up) and optimized processing parameters (bottom).

indexed as $Al_{10}V$ (above 480 °C). Large conglomerates of intermetallic phase with size above ~ 500 μm were observed after annealing above 500 °C, Fig. 2d.

Microhardness of MSR in as-received state was HV 275. Annealing at 100 °C / 30 min resulted in increase of microhardness to HV 427 which was presumably associated by formation of fine high-

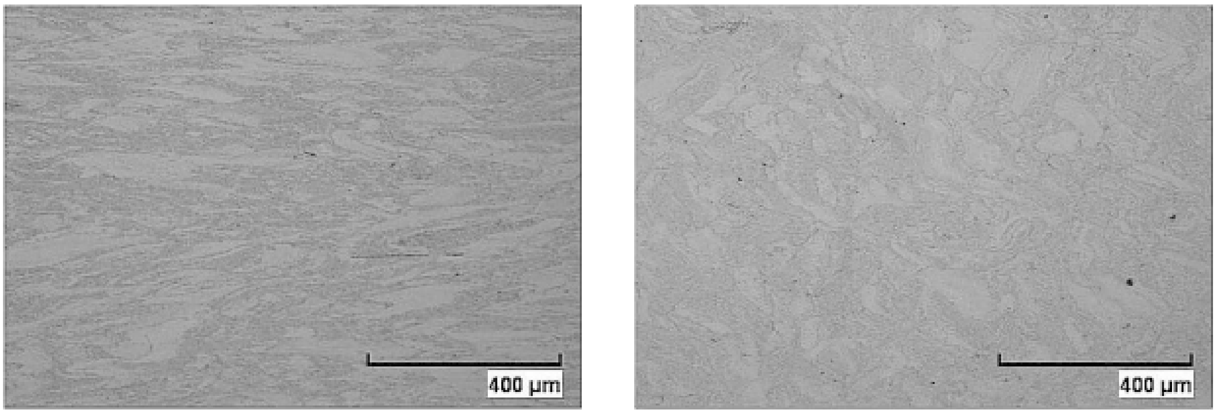

Fig. 4. Longitudinal cross-sections of pre-extruded Al94Fe2V4 MSR subjected to 1 ECAP pass (up) and to 4 ECAP passes via route Bc (bottom) with corresponding microstructures.

strength metastable icosahedral quasicrystalls. At higher temperature (above 400 °C) gradual decrease of HV was observed even below those measured on as-received MSR due to transformation of icosahedral phase into stable intermetallic phases and their coarsening and agglomeration. These results are reported in [2]. Therefore the temperature of ~480 °C represents an upper limit for consolidation of these MSR if expected structure and properties are to be preserved. Thus the experimental compaction trials with MSR (both hot extrusion and ECAP) were performed at 450 °C, which was the minimum temperature enabling extrusion without destroying the die (tool load limit).

3.2. Consolidation

Table 2 represents the effect of temperature on breakthrough pressures for ECAP and DE of ultrafine Al powder. As expected, due to reduction of flow resistance of deformed material with increasing temperature the breakthrough pressure decreases. The values recorded for ECAP were far lower (about 6-7 times) in comparison with DE (extrusion ratio 11:1) performed at the same temperatures. This confirmed the assumption that redundant normal stresses were significantly reduced at ECAP. The highest pressure of 800 MPa in this case was recorded for the lowest temperature of 200 °C. To attain the same pressure in case of DE, the temperature had to be increased up to 500 °C. It is important to note that 800 MPa is typical pressure limit for extrusion tools used in industrial conditions. The extrusion of powder was not possible below 350 °C, where breakthrough pressures approached laboratory tool load limits of ~1400 MPa [3].

The longitudinal section of particulate pre-compacted samples submitted to 1 ECAP pass is illustrated in Fig. 3. The shape of front part of the specimen reveals that friction on channel walls significantly contributes to the art of overall deformation. In theoretical case when friction is not considered shear would produce deformation resulting in inclination of the front plane by 45°. In reality front plane is tilted by about 30-35° what indicates that friction force between container and bottom channel wall is significantly higher than friction force on upper channel wall. As a result of heterogeneous deformation throughout the cross-section, i.e. gradient of straining and strain rate between lower and upper wall of outlet channel, consolidation cracks may form if the processing parameters are not properly adjusted [6].

First ECAP trials for compaction of $Al_{94}Fe_2V_4$ MSR were not successful because of insufficient green density of CIPed MSR. The absence of normal stresses led to large voids and cracks in compacted sample, although some regions were satisfactorily compacted exhibiting sound metallurgical bonds between chopped ribbons. Therefore, further ECAP experiments were done using MSR, which were pre-extruded at very low extrusion ratio (4:1) in order to enable breakthrough at 450 °C.

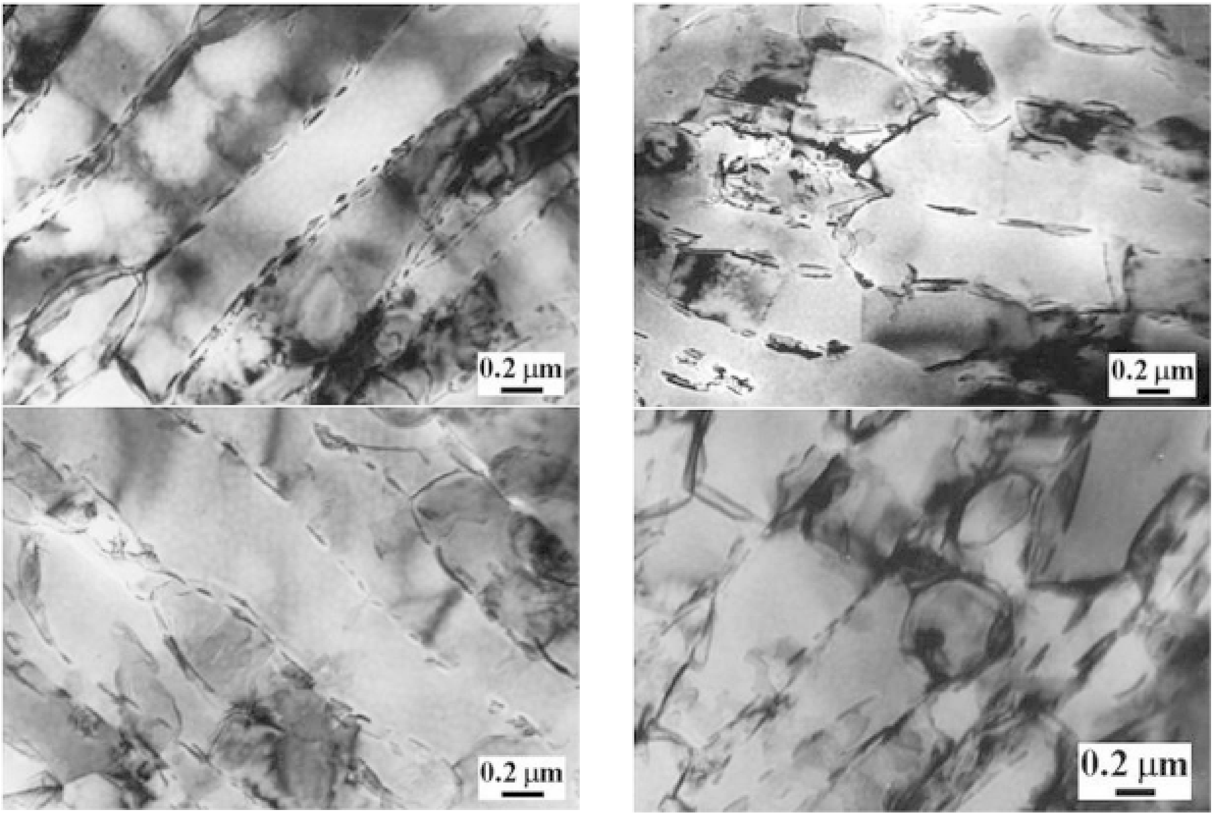

Fig. 5. TEM microstructures of Al powder processed by single ECAP pass at 200 °C (a) 350 °C (b), by direct extrusion 11:1 at 500 °C (c) and by four ECAP passes at 350 °C (d).

Fig. 4 illustrates longitudinal cross-sections of such pre-extruded samples filled in Cu container and subjected to single ECAP pass and four ECAP passes according to route Bc, respectively. Macroscopic pores or cracks were not observed in both cases. As can be seen, the front plane of the multiply pressed sample is rather perpendicular to ECAP pressing direction. This is in good agreement with shearing characteristics associated to different routes [7], whereas the initially cubic element is fully recovered after 4*n* passes (when *n*= 1, 2, 3, etc.) if the route Bc is used. This approach may also result to suppression of strong texture after DE due to higher and more complex shear deformation introduced into the material by multiple pressing and rotation of the specimen, whereas the grains became more equiaxially oriented, as shown in Fig. 4b. The similar behavior was observed also for ECAP compaction of powders (Fig. 5d).

3.3. Microstructure observations

TEM micrographs of Al powder after 1 ECAP pass performed at 200 °C is shown in Fig. 5a. Microstructure consists of well-deformed grains elongated in the shear stress direction throughout the entire cross-section of the specimen. The oxides envelopes initially forming continuous cover of each grain are torn off and relatively homogeneously dispersed at grain boundaries enabling good metallic bonding between Al cores. A slightly finer microstructure was observed in case of consolidation at lower temperatures due to higher deformation work induced during consolidation process (compare Figs. 5a and 5b). Very similar microstructure to that one achieved by ECAP of Al powder at 350 °C was achieved by DE at extrusion ratio 11:1 however at far higher temperature of 500 °C, Figs. 5b and 5c).

Excellent metallurgical bonding was detected also in case of chopped AlFe2V4 MSR. As can be

Table 3. Breakthrough pressures, densities and microhardness obtained during consolidation of AlFe2V4 MSR via various methods at 450 °C.

Consolidation method	DE, ER 11:1	DE, ER 4:1	1xECAP	4x ECAP, Bc
Breakthrough pressure [MPa]	1400	1280	210	210-320
Relative density [%]	89,8	87,1	91,8	92,4
HV microhardness	203	197	210	226

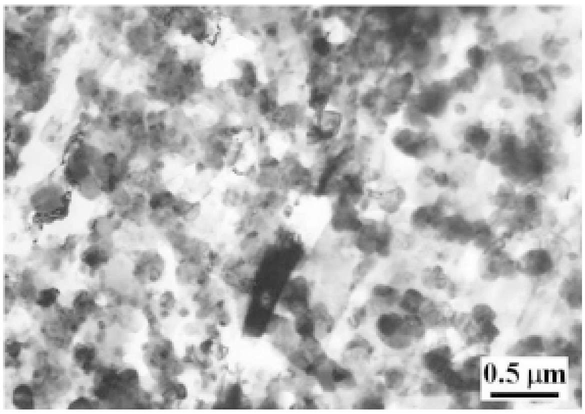

Fig. 6. TEM micrograph of Al94Fe2V4 MSR compact after single ECAP pass at 450 °C.

seen in Fig. 6 no distinctive phase transformations took place on compaction of MSR via single ECAP at 450 °C and the microstructure is similar to that obtained in as-received ribbons. No coarsening of nano-metric particles, even slight refining of the structure due to induced deformation was observed.

3.4. Density measurements

The densities of Al powder compacts after single ECAP pass were very close to theoretical density (Table 2). Values in the range of 2.65 – 2.67 gcm^{-3} in dependence on consolidation temperature were attained. As it was expected, multiple pressing using route Bc resulted in increasing of density up to 2.7 g.cm^{-3}.

Relative densities of MSR compacts are summarized in Table 3 for various consolidation methods. It is shown, that relative density of ECAP compacts is slightly higher (2%) than that obtained for extruded samples, whereas multiple ECAP passes resulted only in marginal density improvement.

3.5. Mechanical properties

Table 2 summarizes HV microhardness of Al powder compacts consolidated at various temperatures via ECAP and direct extrusion. The highest microhardness of HV 102.6 was found for powders compacted via ECAP at the lowest temperature of 200 °C. This value is comparable with microhardness obtained for powders extruded at 350 °C. Increasing compaction temperature resulted in slight decrease of compact's microhardness for both ECAP and extrusion processes, although this decrease was more pronounced in case of extruded samples, due to relaxation processes which start at higher temperatures. The obtained HV values correspond to UTS at the level of ~300 MPa that is extraordinary high if compared to pure Al ingot processed by ECAP (HV 32.2, UTS=64 MPa) or to plain Al powder processed by back pressure ECAP (HV 52.7, UTS=160 MPa) reported in [8]. It is presumably due to the reinforcing effect of fine dispersoids arising from fragmentation of oxides presenting at the large surface of ultrafine Al powder grains.

Single ECAP pass of pre-compacted AlFe2V4 MSR resulted in ~ 5% improvement of HV microhardness in comparison to extruded MSR (Table 3). Multiple ECAP provided further improvement of this value, whereas four passes increased HV microhardness by additional ~ 7%.

4. CONCLUSIONS

It has been shown that preparation of sound profiles made from rapidly solidified Al-based discrete particles is feasible using ECAP method. Following conclusions can be presented:

- Breakthrough pressures needed for Equal Channel Angular Pressing (ECAP) of ultra-fine 1 μm Al 99,7% powder and $Al_{94}Fe_2V_4$ melt-spun ribbons were significantly reduced in comparison to direct extrusion process with extrusion ratio 11:1 at the same temperature;

- This allows successful synthesis of discrete particles of both materials into bulk profiles at much lower temperatures than possible with conventional direct extrusion process;
- Well deformed particles and good metallurgical bonding between them throughout the entire cross-section were observed in compacted profiles even after one ECAP pass;
- Microstructure after one ECAP pass was similar to that observed on directly extruded compacts at extrusion ratio 11:1 but was achieved at far lower temperatures and compaction pressures, respectively;
- Density and HV microhardness attained after single ECAP pass was comparable or even higher than that achieved at conventional extrusion, whereas multiple ECAP results to further improvement of these properties.

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REFERENCES

[1] H. Kimura, K. Sasamori and A. Inoue // *Mater. Sci. Eng. A* **294-296** (2000) 168.

[2] J. Nagy, M. Balog, K. Izdinsky, F. Simancik, P. Svec and D. Janickovic // *Int. J. Mat. & Product Tech.* **23** (2004) 79.

[3] M. Balog, J. Nagy, K. Iždinský and F. Simančík // *Int. J. Mat. & Product Tech.* **23** (2005) 70

[4] C.H. Shek, G. He, Y. Bian Y., G.L. Chen and J.K.L. Lai // *Mater. Sci. Eng. A* **357** (2003) 20.

[5] A. Inoue // *Progress in Materials Science* **43** (1998) 365.

[6] Roberto B. Figueiredo, Paulo R. Cetlin and Terence G. Langdon // *Acta Materialia* **55** (2007) 4769.

[7] M. Furukawa, Y. Iwahashi, Z. Horita, M. Nemoto and T.G. Langdon // *Mater. Sci. Eng. A* **257** (1998) 328.

[8] K. Xia and X. Wu // *Scripta Materialia* **53** (2005) 1225.