

Influence of Sintering Conditions on Compacted Rapidly Solidified AlFeCrSiTi Alloys

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This work is devoted to the preparation of AlFeCrSiTi alloys by powder metallurgy using melt atomization and spark plasma sintering. Conventional aluminium alloys are characterized by low density but their main problem is thermal stability. The strengthening fine precipitates coarsen at temperature above 300 °C in few minutes, which leads to decrease of mechanical properties. As a solution for this problem, it is suggested to prepare Al–TM (transition metal) alloys by rapid solidification, which leads to presence of big amount of fine Al–TM intermetallics slowing down diffusion and suppressing recrystallization because the Al–TM precipitates are predominantly located at the grain boundaries and triple junction of grains. The rapid solidification process also causes formation of metastable phases, e.g. supersaturated solid solution and quasicrystals. Decomposition of both these phases brings feasibility of self-healing properties to the alloy. Self-healing behaviour of alloy means the ability to close and heal micro- or nanoscaled crack present in material. In case of rapidly solidified alloys, the expected mechanisms are precipitation from supersaturated solid solution or decomposition of quasicrystals accompanied by change of size and shape of intermetallic particles. Microstructure and selected mechanical properties of bulk AlFeCrSiTi alloy were studied by transmission electron microscopy, X-ray diffraction, and compressive testing.

DOI: [10.12693/APhysPolA.134.738](https://doi.org/10.12693/APhysPolA.134.738)

PACS/topics: 61.66.Dk, 61.05.cp, 62.20.mt

1. Introduction

Aluminium alloys are used mainly for highly stressed components in applications, where their low density is needed, e.g. in aerospace and automotive industry. Among their benefits there are low density and high tensile strength (up to 700 MPa). Mechanical properties are stable only at low temperatures up to 270 °C [1, 2]. Low thermal stability of common Al alloys is due to relative high diffusion coefficients of their alloying elements (Cu, Zn, Mg) in solid aluminium [2–4]. Processing of Al alloys by rapid solidification techniques has several advantages — e.g. structure refinement leading to increase of strength or forming of metastable phases like supersaturated solid solution and quasicrystalline phases. Thermally stable bulk ultrafine-grained aluminium alloys can be prepared by two-step powder metallurgy route — in the first step, powder is prepared by rapid solidification or by mechanical alloying. Following step is compaction of powder by hot-isostatic pressing, hot extrusion, spark plasma sintering or other techniques of powder metallurgy [5]. Rapidly solidified aluminium alloys have usually fine-grained microstructure formed by aluminium matrix containing metastable non-equilibrium phases and finely dispersed intermetallic phases [6]. Compaction of rapidly solidified powders by various methods can preserve the fine microstructure and so strength of material. Appropriate microstructure formed by fine grains with grain boundaries blocked by stable precipitates provide the material with ther-

mal stability [7]. Moreover, preserving the metastable phases into bulk can enrich the material by possible self-healing properties, which means the ability of material to close and heal crack. There are two possible mechanisms to achieve this behaviour. The first one is precipitation from supersaturated solid solution and it was already proven for commercial Al alloy heat treated to under-aged state [8]. It was shown that the precipitates will form predominantly on energetically rich places like cracks [9]. The other possible self-healing mechanism is based on decomposition of quasicrystals. This phase transformation is accompanied by change of size and shape of intermetallics particles [10]. The quasicrystalline arrangement is very close packed. On the other hand, the products of quasicrystals decomposition are common intermetallic phases (for decomposition of Al–Cr quasicrystals it is monoclinic $\text{Al}_{13}\text{Cr}_2$). Increase of volume of intermetallic particle can lead to closing of the crack in the material.

In this work, the AlFe₂Cr₆Si₁Ti_{1.5} alloy is prepared by powder metallurgy using melt atomization followed by compaction by spark plasma sintering method. The influence of the initial powder particle size on phase composition, microstructure and room temperature compression strength of compacted AlFe₂Cr₆Si₁Ti_{1.5} alloy was examined.

2. Experimental

The AlFe₂Cr₆Si₁Ti_{1.5} alloy of intended composition was prepared by melting of pure aluminium and silicon with Al–Cr, Al–Ti, and Al–Fe master alloys in an electric resistance furnace in argon atmosphere. In the next step, the AlFe₂Cr₆Si₁Ti_{1.5} alloy was melted in induction furnace and gas-atomized by high-pressure nitrogen

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(500 kPa), forming rapidly solidified powder. Prepared powder was sorted into fractions with particle sizes: under 63 μm , 63–125 μm and above 125 μm . It can be expected that each fraction has been solidified with different quenching rate, which is reflected in phase composition of each fraction mainly on content of metastable phases. There is also different surface to volume ratio of the particles, which has an influence of the sintering conditions. Samples of each powder fraction were compacted by spark plasma sintering method at temperature of 500 °C for 15 min. The pressure was set at 48 MPa and the sintering was carried out in continuous mode.

Microstructure of compact samples (after grinding, polishing and etching by hydrofluoric acid with concentration of 0.5 vol.%) was observed by the metallographic optical microscope Olympus PME3. Residual porosity of sintered materials was measured using Image J software from optical micrographs. Microstructure of powder samples was observed by SEM TESCAN VEGA 3 LMU with BSE detector. The phase composition was evaluated using a PANalytical X'Pert Pro X-ray diffractometer using the HighScore Plus software and PDF2 database. Thin foils for TEM were prepared by grinding until final thickness down to 50–80 μm and by subsequent electrolytic polishing in mixture of HNO_3 and methanol (1:3) at –20 °C with final ion polishing by Gatan PIPs. The samples were investigated by transmission electron microscope EFTEM JEOL 2200 FS. Compression tests on compact samples were performed using testing machine LabTest 5.250SP1-VM. Cubic samples with size of 3 mm were used. The testing direction of compression tests was similar to uniaxial pressing direction during compaction of bulks. Each compression experiment was repeated 3 times.

3. Results and discussion

Microstructure of different powder fractions of AlFe2Cr6Si1Ti1.5 alloy is given in Fig. 1. The smaller the particles are, the finer the microstructure is. It is in agreement with assumption that smaller particles achieve higher cooling rates during solidification process.

Microstructure of compact AlFe2Cr6Si1Ti1.5 alloys from various powder fractions are shown in Fig. 2. XRD patterns of AlFe2Cr6Si1Ti1.5 alloys from various powder fractions are shown in Fig. 3. All powder fractions contained α -Al, stable intermetallic phase $\text{Al}_{13}\text{Cr}_2$ and quasicrystalline phase $\text{Al}_{95}\text{Fe}_4\text{Cr}_1$ described as icosahedral in [11]. The $\text{Al}_{84}\text{Cr}_{15}$ quasicrystalline phase described in [12] was observed only in rapidly solidified powder with the finest particle size fraction (under 63 μm) due to highest quenching rate of this fraction enabling to form highly alloyed metastable phase. Residues of this phase were detected in the compacted sample prepared from the finest powder, but the majority was decomposed during compaction by SPS. Evolution of $\text{Al}_{13}\text{Fe}_4$ phase during compaction can be also observed in Fig. 3. This phase is formed by decomposition of both super-saturated solid solution of Fe in Al matrix and $\text{Al}_{84}\text{Cr}_{15}$

quasicrystalline phase. At elevated temperatures quasicrystalline phases are transformed into more thermodynamically stable crystalline intermetallic phases (mainly $\text{Al}_{13}\text{Cr}_2$ and $\text{Al}_{13}\text{Fe}_4$) [4]. This transformation is accompanied by increase of size of intermetallic particle and by change of particles morphology [3]. We assume that this process can lead to closing of crack in the material and so provide the material with “self-healing” properties.

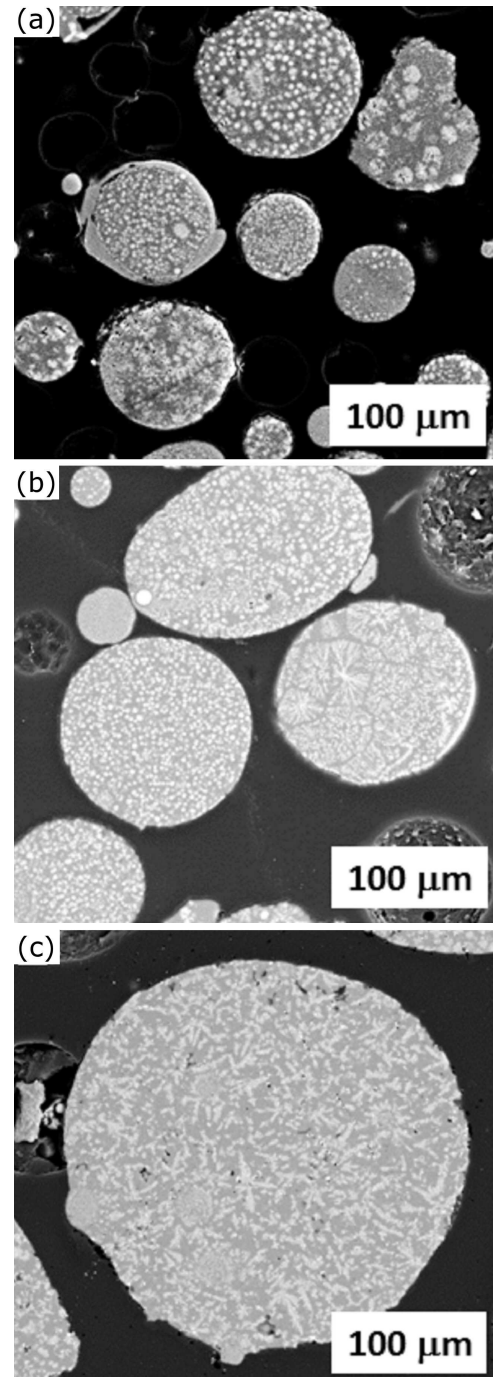


Fig. 1. Microstructure of AlFe2Cr6Si1Ti1.5 powder alloy with fractions: (a) under 63 μm , (b) 63–125 μm , and (c) above 125 μm (SEM).

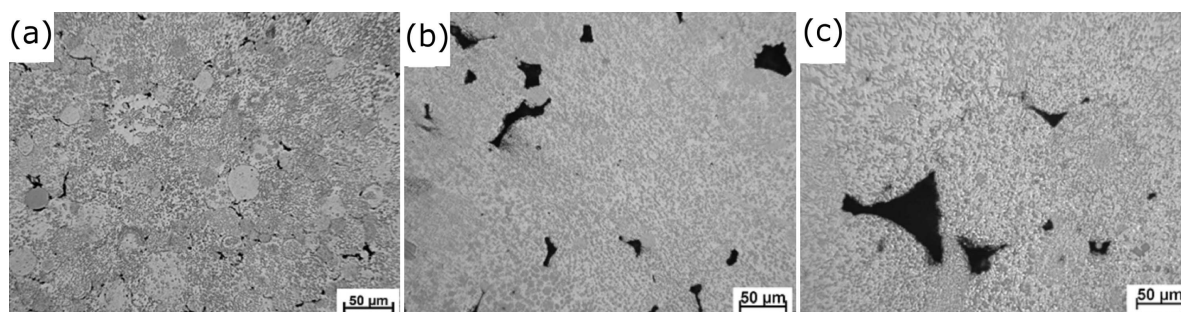


Fig. 2. Microstructure of AlFe₂Cr₆Si₁Ti_{1.5} alloy sintered from powder fraction: (a) under 63 μm, (b) 63–125 μm, and (c) above 125 μm (LOM).

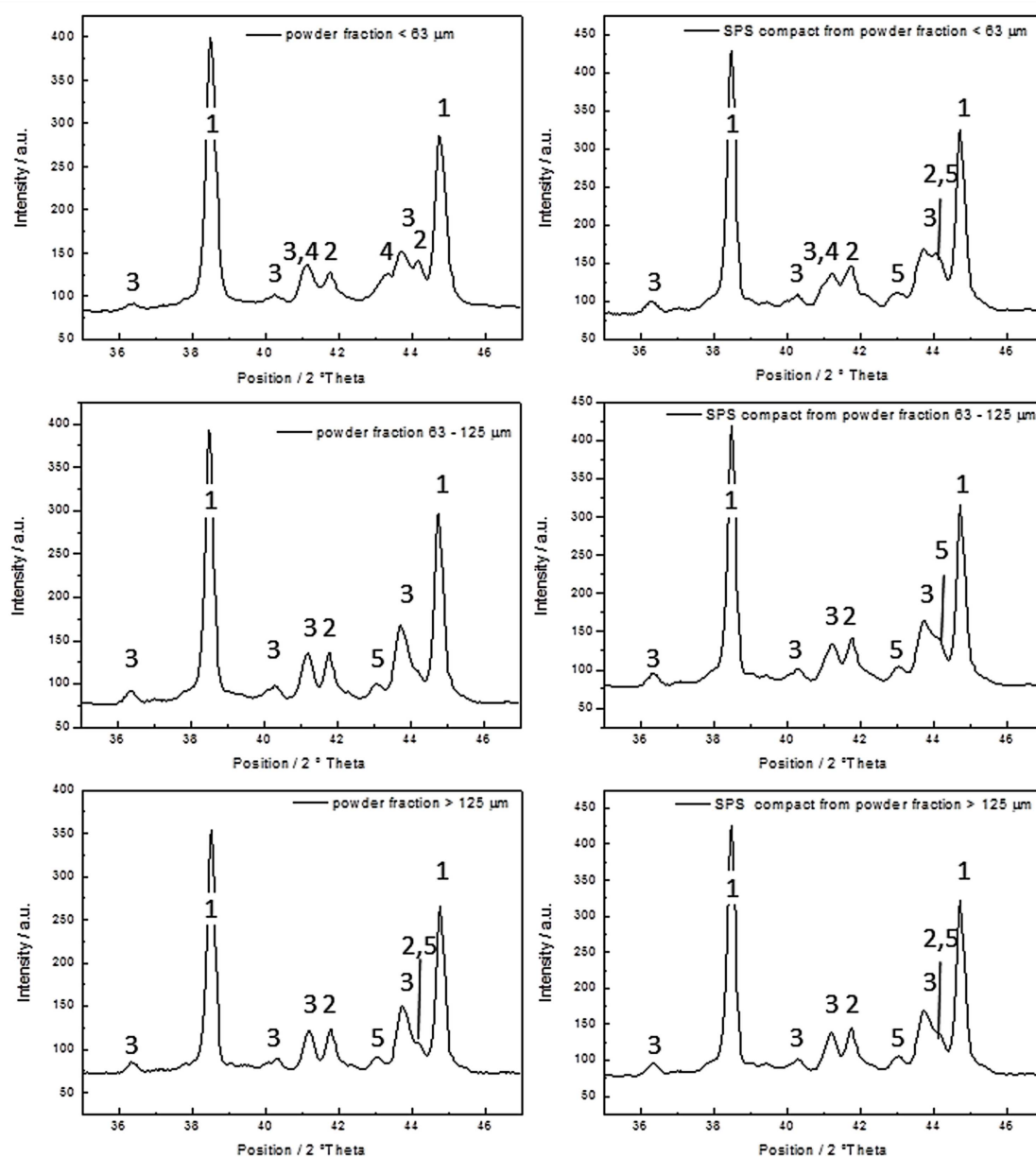


Fig. 3. Detailed XRD pattern of AlFe₂Cr₆Si₁Ti_{1.5} alloy (phases: 1 — Al, 2 — Al₉₅Fe₄Cr₁, 3 — Al₁₃Cr₂, 4 — Al₈₄Cr₁₅, 5 — Al₁₃Fe₄).

No Ti- and Si-containing phases were identified in the XRD patterns, probably due to a small amount of these elements in the initial powders or close atomic radii of alloys elements and so dissolving of the titanium in quasicrystalline phases or aluminium (dissolving of the silicon in phase with iron). This assumption is in agreement with data reported by Kimura et al. [4], who described various ternary Al–Fe–Cr–Ti quasicrystalline phases.

The microstructures of compacted AlFe2Cr6Si1Ti1.5 alloys were investigated and documented by transmission electron microscope (Fig. 4). The microstructures of alloys composed of finely dispersed particles of intermetallic phases (IP — darker parts) in the α -Al matrix (lighter parts). The intermetallic particles are located predominantly at the grain boundaries, frequently they are presented in form of clusters. It complicates their better description e.g. by SAED by overlaying individual particles and matrix. The main difference among materials prepared from various initial particle size is the grain size of the aluminium matrix, which is given in Table I.

The average size of coherently diffraction domains of aluminium (Table I) estimated from XRD patterns by the Scherrer calculator is about $0.1 \mu\text{m}$ for all materials. The average grain size measured from TEM images is between 1 and $2.6 \mu\text{m}$. This disagreement of obtained values can be explained by the fact that from XRD the size of coherently diffracting domains is estimated, which corresponds e.g. to subgrain size. On the other hand, the value determined from TEM images corresponds to the grains size. In our case, the subgrains are not visible by TEM, and the difference can be caused by presence of clusters of intermetallics on the grain boundaries distorting the matrix lattice or by measuring error. Due to submicrometer scale, it is not possible to prove the presence of subgrains by EBSD.

Mechanical properties of material prepared by powder metallurgy are influence by two contradictory factors. The first one is grains size. With decrease of grain size, the values of yield stress should be higher according to the Hall–Petch relationship. The other factor is presence of oxide layers on the surface of initial powder particles. They could serve as strengthening particles (so-called oxides dispersion strengthening = ODS). More likely, they form the weak parts at grain boundaries and so decrease the cohesion of sintered particles. Therefore, the effect of oxide particles is not unambiguous. The values of compressive yield strength of compacted alloys are shown in Table II. The values are similar within ex-

TABLE I

Average values of the Al grain size, size of coherently diffracting domains and compression yield strength of AlFe2Cr6Si1Ti1.5 alloys

Particle size fractions [μm]	Powder Al subgrain size (XRD) [nm]	Bulk Al subgrain size (XRD) [nm]	Bulk Al grain size (TEM) [μm]	Yield strength in compression [MPa]
under 63	60 ± 20	100 ± 30	1.0 ± 0.2	242 ± 4
63–125	100 ± 20	130 ± 30	1.9 ± 0.3	246 ± 4
above 125	100 ± 20	120 ± 20	2.6 ± 1.3	235 ± 12

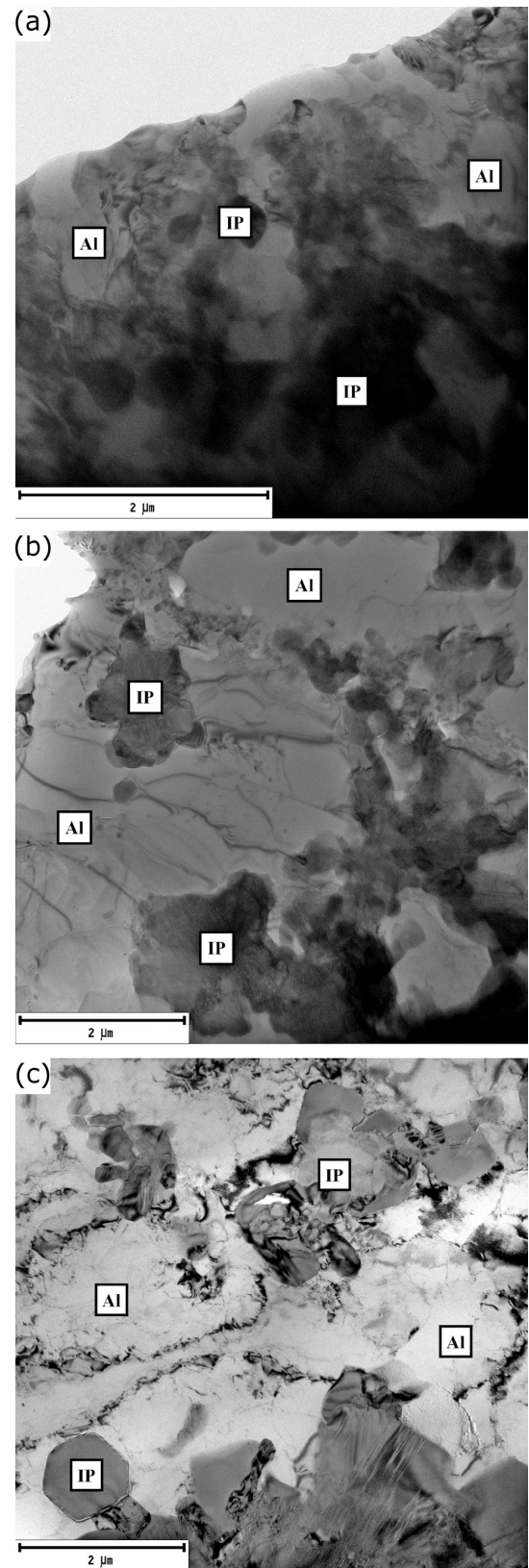


Fig. 4. TEM cross-section micrographs (Al and intermetallic phases $\text{Al}_{13}\text{Cr}_2$, IP) are marked of the RS Al–Fe–Cr alloys compacted from particle size fractions: (a) under $63 \mu\text{m}$, (b) $63\text{--}125 \mu\text{m}$ and (c) above $125 \mu\text{m}$.

perimental errors. It means that no strengthening due to the Hall–Petch relationship was observed for the material prepared from the finest powder fraction. It can be explained by presence of highest amount of oxide particles. They do not cause ODS but are probably the weak parts of sintered material. Nevertheless, materials prepared in our research had lower yield strength as analogous materials published in literature [5, 6] but higher than material prepared from the same powder by hot extrusion [3].

TABLE II

Values of yield strength for comparable materials

Alloy composition	Yield strength [MPa]	Reference
AlFe2Cr6Si1Ti1.5	120	[3]
Al95Cr3.1Fe1.1Ti0.8	547	[5]
Al93Fe3Cr2Ti2	544	[6]
Al92.5Ti2.5Fe2.5Cr2.5	540	[6]

Materials prepared from different powder fraction have also different residual porosity that was 0.6 vol.% for the finest fraction, 2.8 vol.% for the fraction 63–125 μm and 4.0 vol.% for the fraction above 125 μm . The increase of porosity can be explained by presence of hard oxide layers on the surface of initial particles that do not allow particles to deform during sintering. Because of that the filling is better with smaller particles.

4. Conclusion

The AlFe2Cr6Si1Ti1.5 alloy was successfully prepared (in form of bulk materials, with low residual porosity) by powder metallurgy using melt atomization and spark plasma sintering under the following conditions: temperature of 500 °C and sintering time for 15 min. Three different powder granulometric fractions were used for compaction (less than 63 μm , 63–125 μm and above 125 μm). All three alloys prepared in this way were formed by α -Al solid solution with intermetallic phases Al₁₃Cr₂ and Al₁₃Fe₄ and quasicrystalline intermetallic phase Al₉₅Fe₄Cr₁. Moreover, the finest fractions of powder contained quasicrystalline intermetallic phase Al₈₅Cr₁₅, that

it was partially decomposed during the compaction process forming stable intermetallic phases. By room temperature testing, all alloys exhibited good yield strength comparable with analogous materials. The best value of yield strength was obtained for the material prepared from powder fraction 63–125 μm , but the difference was not significant. The future research will be focused on the alloy prepared from the finest powder fraction as it contains two quasicrystalline phases, which gives the material potential for possible self-healing behaviour.

Acknowledgments

This research was supported by Czech Science Foundation, project No. GJ17-25618Y.

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