UDK 621.762:669.715 ISSN 1580-2949
Original scientific article/Izvirni znanstveni članek MTAEC9, 46(4)339(2012)

APPLICATION OF POWDER METALLURGY IN THE PROCESSING OF ALUMINIUM SCRAPS WITH HIGH-IRON CONTENTS

UPORABA POSTOPKOV PRAŠNE METALURGIJE ZA PREDELAVO ODPADKOV NA OSNOVI Al Z VISOKO VSEBNOSTJO Fe

Dalibor Vojtěch, Filip Průša

Department of Metals and Corrosion Engineering, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic
dalibor.vojtech@vscht.cz

Prejem rokopisa – received: 2011-10-20; sprejem za objavo – accepted for publication: 2012-03-12

The Al-14Si-8Fe and Al-22Si-8Fe-1Cr (*w*/%) alloys were prepared via melt centrifugal atomization and compaction at a pressure of 6 GPa. The resulting alloys were porosity-free with good contacts between the particles. The structures were very fine and consisted of primary α(Al) dendrites, eutectic silicon and the β-Al_5FeSi phase. The Vickers hardness values of the Al-14Si-8Fe and Al-22Si-8Fe-1Cr alloys were (170 ± 10) HV5, (185 ± 16) HV5, respectively. Compressive strength values were 670 MPa and 720 MPa, respectively. Surprisingly, both alloys exhibited a very good plasticity due to the refined structure. The alloys were annealed at 300–400 °C for 100 h to reveal their thermal stability. When the thermal stability of the powder-metallurgy Al-14Si-8Fe and Al-22Si-8Fe-1Cr alloys was compared to that of the casting-piston Al-12Si-1Cu-1Mg-1Ni alloy, the former was found to be superior.

Keywords: aluminium, powder metallurgy, rapid solidification, iron

Zlitini Al-14Si-8Fe in Al-22Si-8Fe-1Cr (*w*/%) sta bili pripravljeni s centrifugalno atomizacijo in hladnim enoosnim stiskanjem s tlakom 6 GPa. Izdelane zlitine so bile brez por z dobrim stikom med delci. Zlitini sta imeli zelo fino mikrostrukturo, ki je vsebovala primarne α(Al)-dendrite, Si-evtektik in fazo β-Al_5FeSi. Trdota zlitine Al-14Si-8Fe je bila (170 ± 10) HV5 in (185 ± 16) HV5 zlitine Al-22Si-8Fe-1Cr. Tlačna trdnost zlitin je bila 670 MPa oziroma 720 MPa. Presenetljivo sta imeli obe zlitini tudi odlično plastičnost zaradi rafinirane strukture. Zlitini smo žarili 100 h pri 300–400 °C, da bi ugotovili njuno termično stabilnost. Ugotovili smo, da je termična stabilnost izdelanih P/M-zlitin Al-14Si-8Fe in Al-22Si-8Fe-1Cr superiorna v primerjavi z ventilsko litino Al-12Si-1Cu-1Mg-1Ni.

Ključne besede: aluminij, metalurgija prahov, hitro strjevanje, železo

1 INTRODUCTION

Aluminium alloys exhibit a relatively high strength-to-weight ratio and good corrosion resistance. This makes them attractive for automotive and aerospace industries. In the recycling of aluminium, various grades of the Al-containing scraps are processed. In addition to water, oils, plastics and other non-metallic contaminants, the main metallic impurity in the Al scraps is iron (Fe). The iron contents depend on the actual scrap grade that can exceed the mass fraction (*w*/%) 10 %. Unfortunately, iron very negatively influences the mechanical properties of Al alloys, because it forms hard and brittle intermetallic phases in the structure, as seen in **Figure 1**. Therefore, the iron contents in most of the commercial, wrought, Al-based alloys must be minimized to a few tenths of *w*/%. Only die-casting Al-Si alloys can contain approximately 1 % of Fe, but the negative effect of the intermetallic phases is balanced with the relatively high cooling rates and fine structures of the castings. In the processing of the Fe-containing Al scraps, the iron contents can be lowered, for example, by magnetic separation before melting or by melting at carefully controlled temperatures to prevent dissolution of Fe in the molten aluminium. These techniques increase the investment and processing costs. For this reason, the Fe-containing Al scraps are significantly cheaper than the Fe-free Al scraps. For example, the price of the scrap

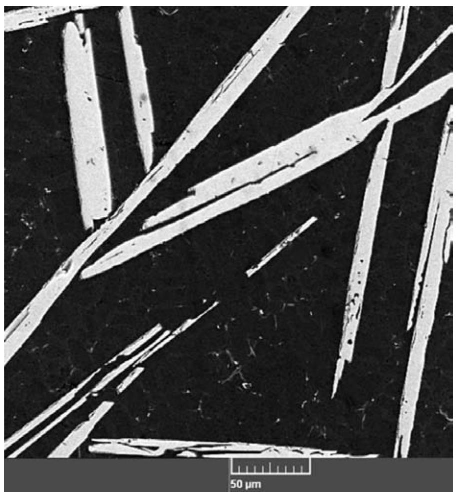

Figure 1: SEM micrograph of the as-cast Al-14Si-8Fe alloy containing large β-Al_5FeSi plates (light) deteriorating the mechanical properties
Slika 1: SEM mikroskopski posnetek litine na osnovi Al-14Si-8Fe, ki vsebuje velike β-Al_5FeSi (svetle) ploščice, vzrok za slabše mehanske lastnosti

containing up to 10 % of Fe is only one third of that of the Fe-free scrap.

In addition to the classic ingot and casting metallurgy of the Al-based alloys, these alloys can also be processed with powder metallurgy (P/M). It is shown in this study that the P/M is a method which enables the preparation of the qualitatively new Al-based alloys containing transition metals, such as Fe, in the concentrations far exceeding those in common casting and wrought alloys.[1] Therefore, aluminium scraps containing high amounts of iron can be processed with this technique. A rapid solidification of a melt, which generally occurs during the powder preparation, refines the structure, reduces the volume fraction of the intermetallic phases and forms new metastable crystalline, quasi-crystalline and amorphous phases.[1] All of these structural features are beneficial for achieving desirable combinations of strength and ductility. Powder compaction is generally performed by pressing and sintering or by hot extrusion.[2]

2 EXPERIMENT

The P/M alloys with the nominal chemical compositions (in mass fractions, *w*/%) of Al-14Si-8Fe and Al-22Si-8Fe-1Cr are studied in this work. The P/M alloys are compared with the commercial, Al-Si-based casting alloy with the nominal composition of Al-12Si-1Cu-1Mg-1Ni. This alloy is used for the pistons of combustion engines and is generally considered as thermally very stable. The P/M alloys were prepared by melting pure elements and master alloys in a vacuum induction furnace under an argon atmosphere. After a sufficient homogenization of the melt was achieved, the melt was poured into a cast-iron metal mould to prepare an ingot of 20 mm in diameter and 150 mm in length. Solidified powder was rapidly prepared with centrifugal atomization, which is schematically shown in **Figure 2**. The alloy ingot was remelted under argon and ejected onto a rapidly rotating graphite wheel (the rotation speed of 30 000 r/min) to produce flake-like particles (**Figure 3**). The dimensions of the powder particles ranged from 0.1 mm to 2 mm with a thickness of approximately 50 μm. The centrifugal atomization technique allows a production of large quantities of powders at low cost.

The powder was then placed into a tungsten-carbide mould and was compacted by uni-axial pressing at an ultra-high pressure of 6 GPa to prepare cylindrical samples of 15 mm in diameter and 5 mm in height. The pressing temperature and time were 450 °C and 1 h, respectively. The casting alloy was provided by an industrial supplier in the form of an ingot with a thickness of 20 mm and a length of 100 mm. The alloy was heat treated by the T6 regime consisting of solution annealing at 510 °C/5 h, water quenching and artificial aging at 230 °C/6 h.[3]

For all of the investigated materials, compressive mechanical properties were measured with an Instron 5882 machine at a deformation rate of 1 mm/min. Vickers hardness tests were performed at room temperature with a 5-kg load. To examine the thermal stability of the alloys, compressive tests were also performed after annealing the samples for 100 h at 300–400 °C, and the development of the Vickers hardness at room temperature was observed to follow the structural changes induced by the long annealing time. The structures of the alloys were investigated using light microscopy (LM), scanning electron microscopy (SEM, Tescan Vega 3) and energy dispersion spectrometry (EDS, Oxford Instruments Inca 350). The phase composition was determined with X-ray diffraction (XRD, X Pert Pro).

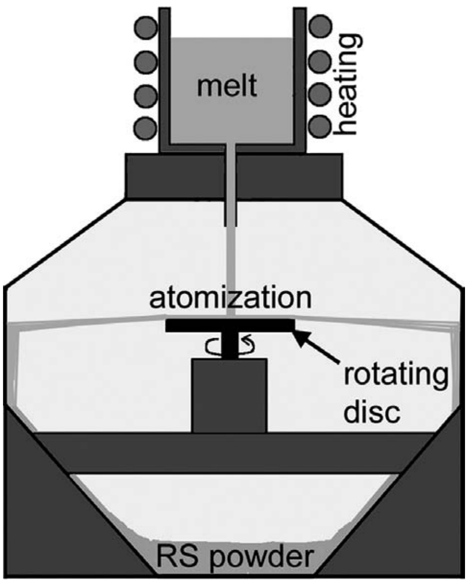

Figure 2: Schematic drawing of the centrifugal atomization used in this study to prepare the P/M alloys

Slika 2: Shematični prikaz centrifugalne atomizacije, ki je bila uporabljena v tej študiji za pripravo P/M zlitin

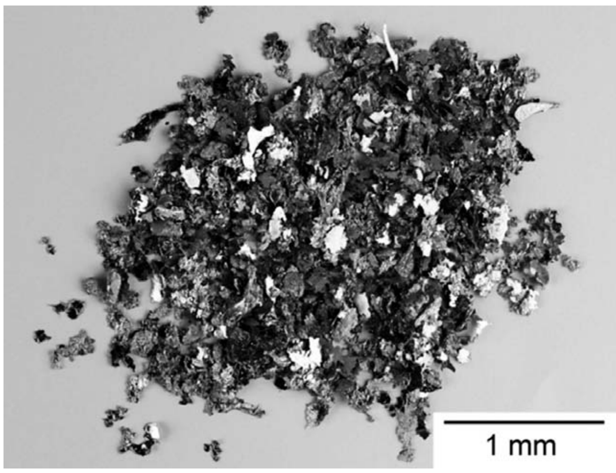

Figure 3: Flake-like powder particles prepared with the centrifugal atomization

Slika 3: Prašni delci v obliki ploščic, izdelani s centrifugalno atomizacijo

3 RESULTS AND DISCUSSION

The structures of the investigated alloys are shown in **Figure 4**. The P/M Al-14Si-8Fe alloy (**Figure 4a**) is dominated by the α(Al) (dark) and β-Al_5FeSi (light) phases. XRD (not shown) also proved the presence of a small volume fraction of eutectic silicon that is hardly seen in an SEM micrograph in the secondary-electron regime. The β-Al_5FeSi phase appears as very fine needles with an average thickness of 2 μm and the length of 8 μm. The P/M Al-22Si-8Fe-1Cr alloy is shown in **Figure 4b**. This alloy has the same phase composition as the previous one, i.e., it contains the β(Al) (dark), β-Al_5FeSi (light) and Si (not seen) phases. The EDS analysis reveals that chromium does not create any new phases. Instead, it is incorporated in the β-Al_5FeSi phase where it substitutes iron atoms. In addition, chromium significantly changes the morphology of the β-Al_5FeSi(Cr) phase from a needle-like to an almost spherical structure. The observed phase composition of the P/M alloys corresponds to the well known ternary equilibrium diagram of the Al-Si-Fe system[4] that is illustrated in **Figure 5**. The structure of the casting Al-12Si-1Cu-1Mg-1Ni (T6) alloy in **Figure 4c** consists of primary α(Al) dendrites (light), α(Al)+Si eutectic and intermetallic phases containing mainly Ni and Al. During the T6 heat treatment of the alloy, plate-like $Al_2CuMgNi$ precipitates were formed which are seen in the TEM micrograph in **Figure 4c**.

By comparing **Figures 1** and **4a**, one can see that the centrifugal atomization of the P/M alloys causes a significant structural refining. This refining is a direct consequence of the rapid solidification occurring during the centrifugal atomization of the melt. In this process (**Figure 2**), the melt stream falls onto a fast rotating wheel, where it is broken into small droplets by the centrifugal force. These droplets are ejected towards the cooled wall of the atomizer, where they rapidly solidify and obtain the typical flake-like shape. It will be shown later that the structural refining has a positive impact on the resulting mechanical properties. It is also important to note that the P/M alloys exhibit almost no porosity and have very good contacts between the particles. Apparently, sufficient diffusion bonding between the

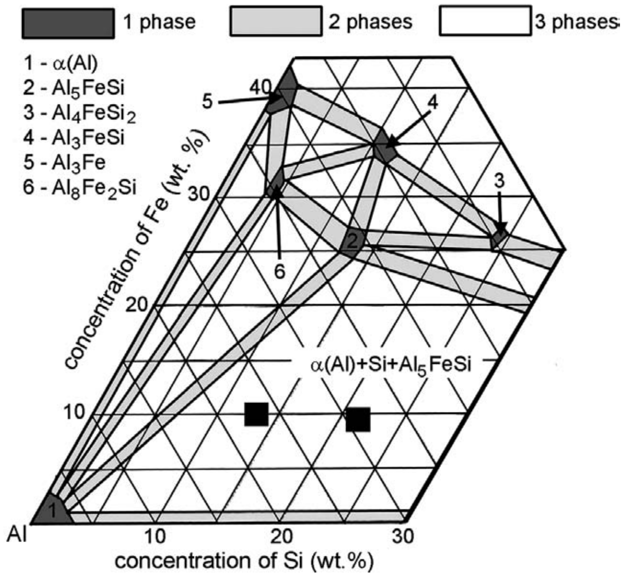

Figure 5: Aluminium corner of the Al-Si-Fe phase diagram[4] (the chemical compositions of the investigated P/M alloys are marked with black cubes)

Slika 5: Al kot v ternarnem faznem diagramu Al-Si-Fe (kemijske sestave preiskovanih litin so označene s črnimi kockami)[4]

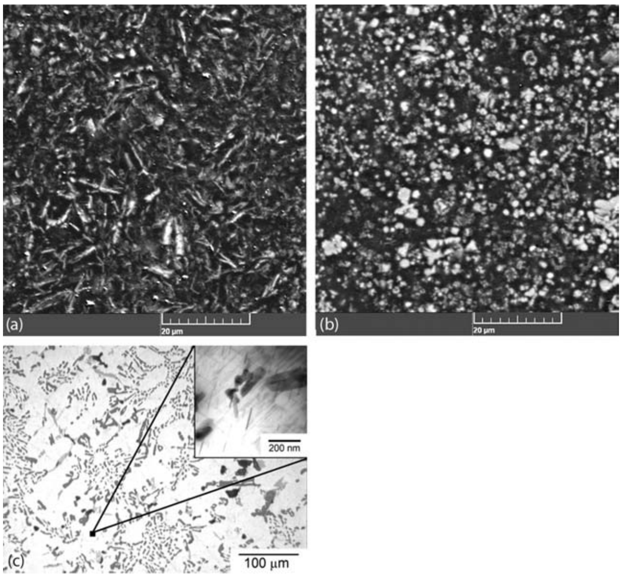

Figure 4: Microstructures of the investigated alloys: a) the PM Al-14Si-8Fe alloy (SEM), b) the PM Al-22Si-8Fe-1Cr alloy (SEM), c) the casting Al-12Si-1Cu-1Mg-1Ni (T6) alloy (LM, TEM)

Slika 4: Mikrostrukture preiskovanih zlitin: a) P/M Al-14Si-8Fe (SEM), b) P/M Al-22Si-8Fe-1Cr (SEM), c) litina Al-12Si-1Cu-1Mg-1Ni (T6) (LM, TEM)

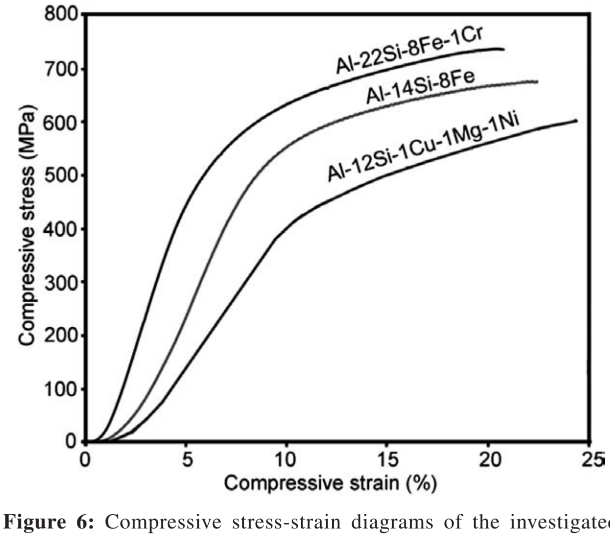

Figure 6: Compressive stress-strain diagrams of the investigated alloys

Slika 6: Diagram odvisnosti med deformacijo in tlačno trdnostjo preiskovanih zlitin

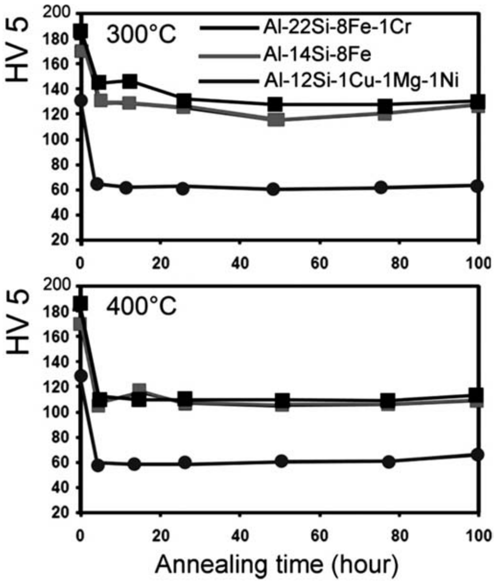

Figure 7: Room-temperature Vickers hardness as a function of the annealing time at 300 °C and 400 °C

Slika 7: Vickersova trdota, izmerjena pri sobni temperaturi v odvisnosti od časa žarjenja pri 300 °C in 400 °C

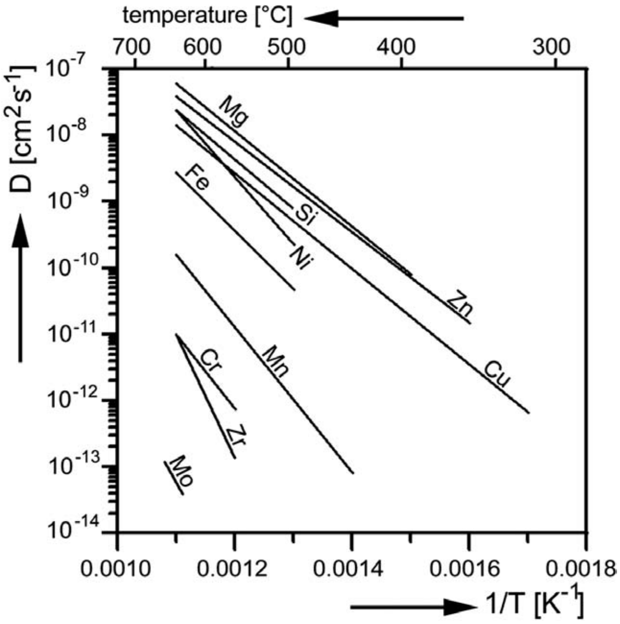

Figure 9: Arrhenius plots of diffusion coefficients D_S, of various metals in Al.[7] Transition metals like Fe have significantly lower diffusion coefficients than the commonly used alloying elements like Cu, Si or Mg.

Slika 9: Arrheniusov diagram difuzijskih koeficientov D_S različnih kovin v Al.[7] Prehodne kovine, kot je Fe, imajo manjše difuzijske koeficiente kot pogosti zlitinski elementi v Al-zlitinah (Cu, Si ali Mg).

particles was induced by the high pressure of 6 GPa used in this experiment. A similar finding was also reported by Cieslak et al.[5]

Figure 6 compares the compressive stress-strain diagrams of the investigated P/M and casting alloys. It is observed that the P/M Al-14Si-8Fe and Al-22Si-8Fe-1Cr alloys exhibit a significantly higher compressive strength (670 MPa and 720 MPa, respectively) than the Al-12Si-1Cu-1Mg-1Ni alloy (600 MPa). Moreover, the P/M alloys also exhibit a higher hardness than their casting counterparts. Vickers hardness values for the Al-14Si-8Fe, Al-22Si-8Fe-1Cr and Al-12Si-1Cu-1Mg-1Ni alloys are (170 ± 10) HV5, (185 ± 16) HV5 and (130 ± 8) HV5, respectively. Higher compressive strength and hardness of the P/M alloys are caused by their observed structural refining due to the rapid solidification (**Figure 4**). An additional contribution to both the hardness and compressive strength is the high volume fraction of the hard phases, namely β-Al_5FeSi, in the structure of the P/M alloys (**Figure 4**). In contrast, the casting alloy contains large α(Al) grains, whose contribution to the Hall-Petch strengthening is negligible (**Figure 4c**). The most pronounced strengthening mechanism operating in this alloy is the precipitation strengthening caused by the semi-coherent $Al_2CuMgNi$ precipitates (**Figure 4c**). The compressive strengths of the P/M alloys investigated in this study (670 MPa and 720 MPa) are higher than the recently reported compressive strengths (→500 MPa) of similar alloys (Al-20Si-5Fe-2(Cu, Ni, Cr)) [6] compacted at 400 °C/1 h, but at a lower pressure of 300 MPa. This suggests that the ultra-high-pressure compaction at 6 GPa positively influences the resulting mechanical properties.

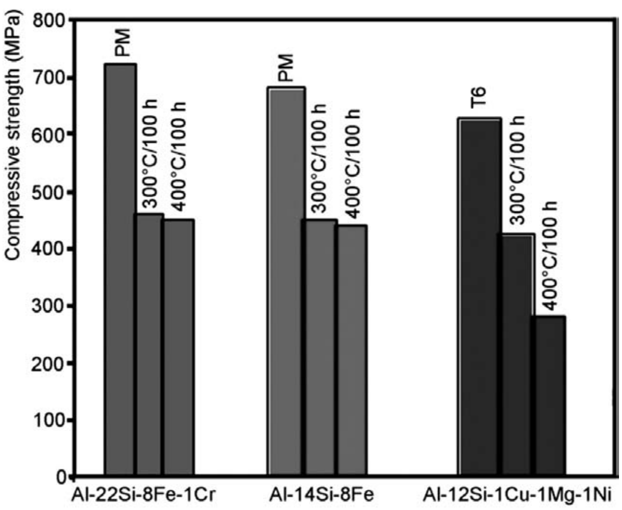

Figure 8: Compressive strength of the alloys as a function of annealing regime

Slika 8: Tlačna trdnost izdelanih zlitin v odvisnosti od režima žarjenja

Another important finding is that both P/M alloys exhibit a very good plasticity, despite the high iron content (**Figure 6**). The alloys with the same chemical composition prepared with the classic casting metallurgy would be extremely brittle due to the presence of the large β-Al_5FeSi plates (**Figure 1**), acting as primary stress concentrators during the compressive loading. The plasticity of the P/M alloys can be attributed to the preparation procedure, including the rapid solidification of the melt. Due to this procedure, the β-Al_5FeSi particles became very fine, short or almost spherical (**Figures 4a** and **4b**). As the stress concentration is proportional to the dimensions of the needles, the refining caused by rapid solidification is able to reduce the local stresses and allow the plastic α(Al) phase to be deformed before the formation of fracture micro-cracks.

Figures 7 and **8** illustrate the thermal stability of the mechanical properties of the investigated alloys. They show the development of the room-temperature Vickers hardness and compressive strength of the alloys during the long-term annealing at 300 °C and 400 °C. Both the hardness and the compressive strength of the P/M alloys decrease during the annealing at 300–400 °C, but these decreases occur much more slowly than in the case of the casting Al-12Si-1Cu-1Mg-1Ni alloy. The P/M alloys retain a relatively high hardness and compressive strength of above 120 HV5 and 450 MPa, respectively, even after the 100 h annealing at 400 °C. One reason for a better thermal stability of the P/M alloys is a lower diffusivity of iron in solid aluminium in comparison with silicon, copper, magnesium and nickel (**Figure 9**).[7] The structural coarsening of the β-Al_5FeSi particles is therefore very slow in the P/M alloys. In contrast, the growth and transformations of precipitates in the casting alloy (**Figure 4c**) occurs fast and, therefore, this alloy softens rapidly during the annealing.

4 CONCLUSIONS

It is demonstrated in this work that the Al-based alloys with a high iron content of 8 % can be successfully prepared with the powder-metallurgy technology that consists of a combination of centrifugal atomization and high-pressure compaction. The resulting alloys have significantly refined structures that have a positive impact on strength, hardness and, particularly, plasticity. The alloys also exhibit excellent thermal stability in comparison with the casting Al-12Si-1Cu-1Mg-1Ni alloy commonly used for the production of the combustion-engine pistons. The classic casting processes cannot be used for the preparation of the high-iron alloys because iron would form large, needle-like β-Al_5FeSi particles, resulting in an extreme brittleness of the as-cast alloys.

Acknowledgements

The authors wish to thank the Czech Academy of Sciences (project no. KAN 300100801) for its financial support of this research.

5 REFERENCES

[1] D. Vojtěch, J. Verner, J. Šerák, F. Šimančík, M. Balog, J. Nagy, Mat. Sci. Eng., A458 (**2007**), 371

[2] L. Shaw, H. Luo, J. Villegas, D. Miracle, Scripta Mater., 50 (**2004**), 921

[3] S. Michna, Aluminium Materials and Technologies from A to Z., Adin, Presov 2007, 375

[4] L. F. Mondolfo, Aluminum Alloys: Structure and Properties, Butter Worths, London 1976, 535

[5] G. Cieslak, J. Latuch, Rev. Adv. Mater. Sci., 18 (**2008**), 425

[6] M. Rajabi, M. Vahidi, A. Simchi, P. Davami, Mater. Charact., 60 (**2009**), 1370

[7] Y. Du, Y. A. Chang, B. Huang, W. Gong, Z. Jin, H. Xu, Z. Yuan, Y. Liu, Y. He, F. Y. Xie, Mat. Sci. Eng., A363 (**2003**), 140