DOI: 10.21062/mft.2022.056  http://www.journalmt.com

# Cast and Rapidly Solidified Aluminium Alloy with the Addition of Deep-Sea Nodules

Pavel Novák (0000-0001-9947-2566), Jakub Vlášek (0000-0001-6854-4360), Alisa Tsepeleva (0000-0003-4999-9890), Alena Michalcová (0000-0002-1225-5380)
Department of Metals and Corrosion Engineering, University of Chemistry and Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic. E-mail: panovak@vscht.cz

**Reduced deep-sea nodules were tested as the alloying mixture for cast and rapidly solidified aluminium alloy. No separation of any metal was used in order to save the processing costs of the deep-sea nodules and to obtain "natural" ratios between the alloying elements. The resulting rapidly solidified alloys contained sharp-edged intermetallics, especially $Al_9Mn_3Si$ phase, which was converted to rounded $Al_{19}Mn_4$ during thermal exposure. The hardness of the ribbons was almost stable during long-term annealing at 300 and 400 °C for 250 h. The alloy can be considered as highly thermally stable.**

**Keywords:** Deep-sea nodules, aluminothermy, aluminium alloy

## 1 Introduction

Deep-sea nodules are polymetallic ores, located in high depts of the world's oceans. Czech Republic has the access to the nodules located in Clarion-Clipperton Zone in Pacific Ocean. The nodules located in this area are manganese-based ones, containing also other elements, such as iron, silicon, nickel or copper. Detailed chemical composition of these nodules is presented here [1]. Since all of the above-mentioned elements have some effect on aluminium's properties, they are used as alloying elements. Manganese is one of the alloying elements with solid-solution strengthening effect and also added as the so-called iron corrector, which influences the shape of the iron-based intermetallic particles [2]. In the case of silicon, the role is mostly in ensuring the castability, leading to the frequently used Al-Si and Al-Si-Cu based alloys [3], and also in age hardening, when used in combination with magnesium [4]. The effect of iron, which is also one of the most abundant metals in the nodules, is rather detrimental, forming brittle needle-like intermetallics with aluminium and silicon [5]. However, in die casting, iron is added to improve the striping of the casting from the die. In rapidly solidified or mechanically alloyed aluminium alloys, the iron addition can be beneficial to increase the thermal stability of the alloys [6]. The thermal stability improvement is also the role of nickel [7], which is the other constituent of the deep-sea nodules. Copper is very widely known as the element ensuring the precipitation hardenability [4]. The idea of this work was to add the reduced deep-sea nodules, which contain the above-mentioned elements and also some minor ones, to aluminium and to describe the resulting microstructure and phase composition in as-cast state and also after the rapid solidification by melt spinning.

## 2 Experimental

The manganese deep-sea nodules with the chemical composition reported in [1] were reduced by aluminothermic process with the 20 % excess of aluminium. The reduced nodules were mixed with aluminium in the molten state and cast by conventional gravity casting, leading to the alloy of a chemical composition presented in Table 1. The chemical composition was determined using X-ray fluorescence (XRF) spectroscopy (PANalytical Axios).

***Tab. 1*** *Chemical composition of the investigated alloy*

| ***Element*** | ***Mn*** | ***Fe*** | ***Si*** | ***Cu*** | ***Ni*** | ***Co*** | ***Zn*** | ***Al*** |
|---|---|---|---|---|---|---|---|---|
| **wt. %** | 4.51 | 0.82 | 1.04 | 0.21 | 0.24 | 0.23 | 0.03 | bal. |

The alloy was processed by melt spinning (MS) using the device developed at UCT Prague. The scheme of the device is listed in [8]. The alloy was melted in the nozzle made of refractory concrete at the temperature of approx. 1000 °C and then ejected on the wheel (made of Cr-Zr bronze) at the rotational speed of approx. 1300 rpm. The phase composition of the alloy both in the as-cast and rapidly solidified state was studied using X-ray diffraction (XRD) by the means of PANalytical X'Petr Pro diffractometer with Cu anode and evaluated using the HighScore Software Package with PDF-2 database. Microstructure was observed after conventional metallographic processing (grinding, polishing) after etching by

Keller's reagent (10 ml $HNO_3$, 5 ml HF, 85 ml $H_2O$). Thermal stability of the rapidly solidified alloy was tested by both short-term annealing at the temperatures of 100 – 600 °C for 1 h followed by Vickers microhardness (HV 0.01) measurement, as well as during long-term tests at 300 and 400 °C for 250 h. In the latter mentioned test, the samples were removed from the furnace in the interval of 50 h and the Vickers microhardness (HV 0.01) was measured.

## 3 Results and discussion

### 3.1 Microstructure and phase composition of the alloy

Microstructure of the as-cast alloy is presented in Figure 1. It is composed of dendrites of aluminium-based solid solution, containing approx. 1.1 % Mn and 0.8 % Si, and three types of intermetallics. The fine ones are located in the inter-dendritic spaces, containing manganese, iron and silicon in a total amount of 10 - 15 wt. % according to the EDS analysis. In reality, the content of the alloying elements can be influenced by surrounding aluminium matrix and hence the real contents could be higher. There are also coarse primary $Al_6Mn$ phases of a needle-like or sharp-edged morphology, where the manganese is partially substituted by iron, as proved by EDS. There are also darker particles inside, having higher content of manganese. The microhardness of the matrix reaches 54 ± 6 HV 0.01, while the microhardness of the phases is 410-440 HV 0.01.

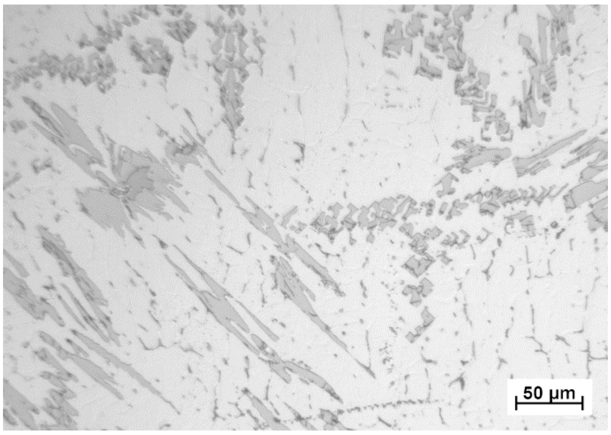


***Fig. 1*** *Microstructure of the investigated alloy in the as-cast state*

X-ray diffraction analysis (Figure 2) confirmed aluminium-based solid solution, $Al_6Mn$ (orthorhombic, Ccmm) and $Al_{19}Mn_4$ (cubic, Pm-3) as the constituents of the alloy. Based on the EDS results we can conclude that the lighter phase is $Al_6Mn$, while the darker inner one is $Al_{19}Mn_4$, because the lighter phase contains lower amount of manganese.

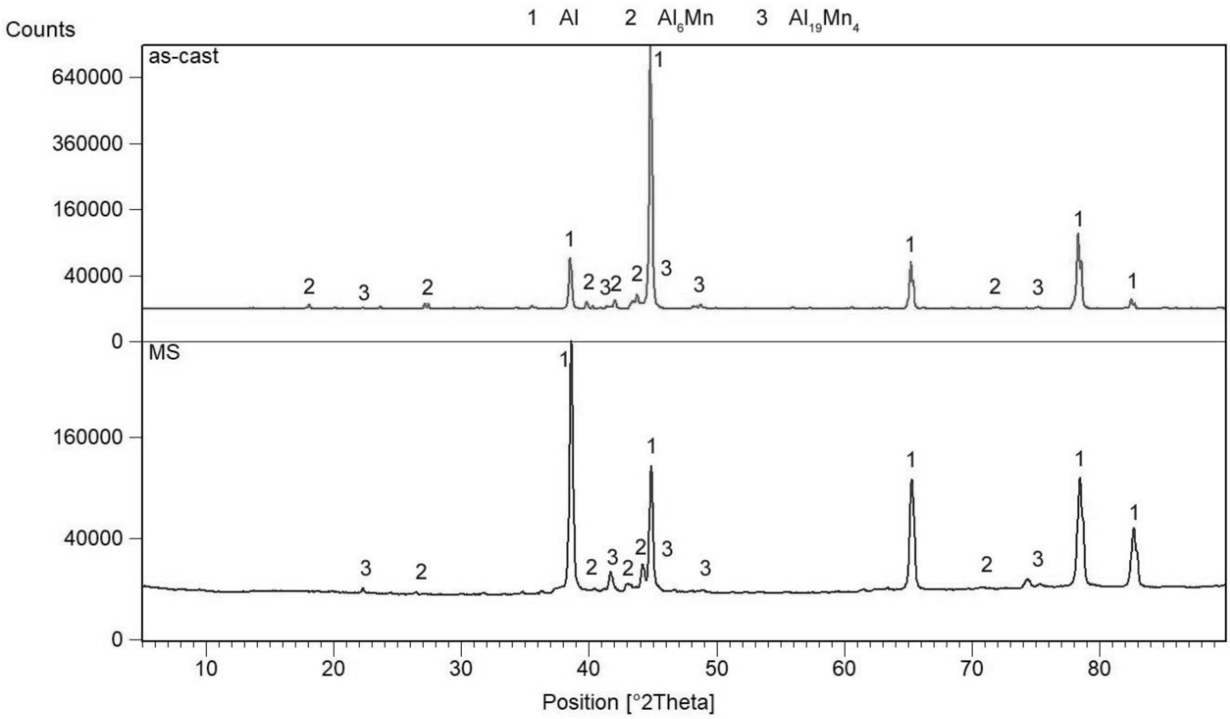


***Fig. 2*** *X-ray diffraction patterns of the as-cast and rapidly solidified alloys*

The rapid solidification by the means of the melt spinning method led to overall refinement of the microstructure of the alloy, see Figure 3. The microstructure is composed of irregular-shaped and needle-like particles in the aluminium-based matrix. According to XRD, the intermetallics are $Al_6Mn$ and $Al_{19}Mn_{14}$ (Figure 2). However, the diffraction pattern of the latter phase is in a strong overlap with $Al_9Mn_3Si$ phase, having similar crystal structure. According to the EDS chemical analysis, the needle-like particles contain high amounts of silicon and hence can be rather determined as $Al_9Mn_3Si$ phase, while the rounded particles are almost silicon-free, being probably $Al_{19}Mn_4$.

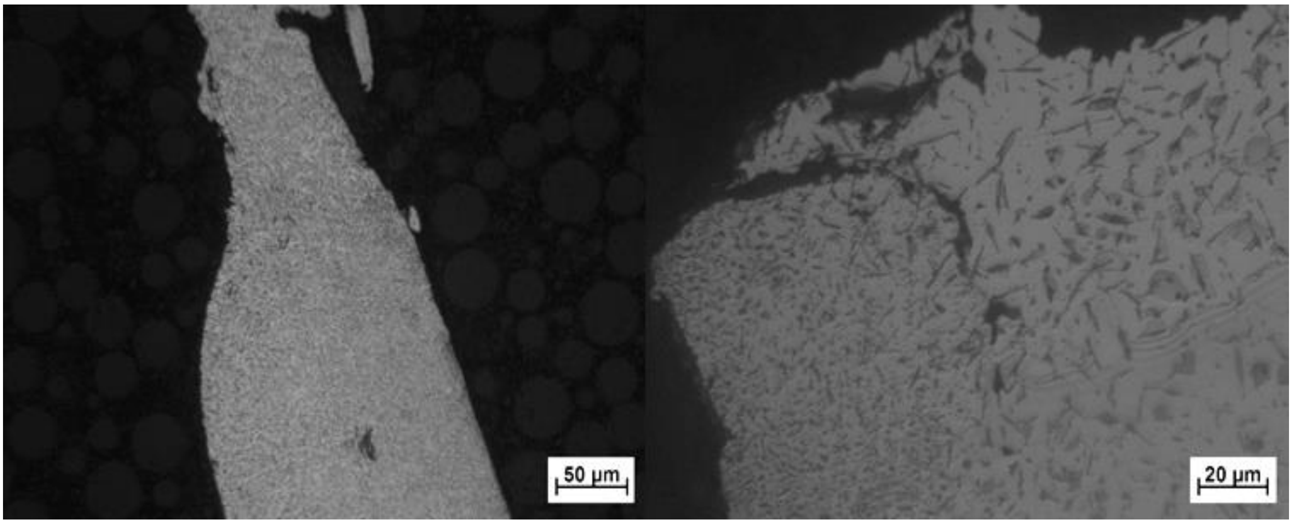


***Fig. 3*** *Microstructure of the investigated alloy after melt spinning (a), detail (b)*

Microhardness of the rapidly solidified ribbon is 94 ± 16 HV 0.01.

### 3.2 Thermal stability of the alloy

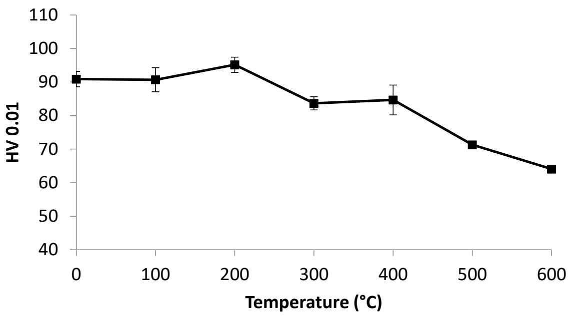


***Fig. 4*** *Microhardness (HV 0.01) vs. temperature of annealing for 1 h*

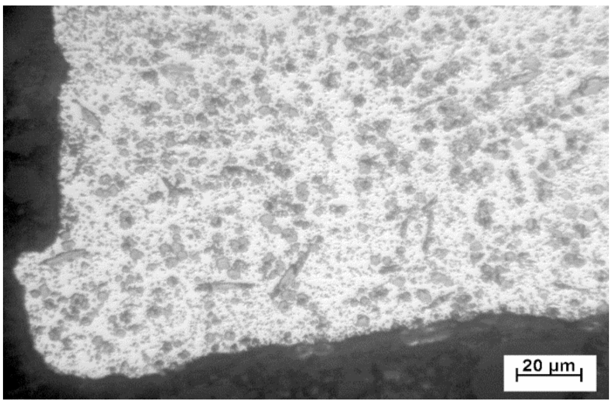


***Fig. 5*** *Microstructure of the alloy annealed at 600 °C for 1 h*

Thermal stability of the alloy was tested by both short-term and long-term annealing. The short-term annealing was carried out at the temperatures of 100 – 600 °C for 1 h. The result is presented in Figure 4. A slight strengthening effect was observed at the temperature of 200 °C, probably being connected with the decomposition of a supersaturated solid solution obtained by rapid solidification. Moreover, microstructure observation of the sample of the ribbon annealed at 600 °C revealed that the spheroidization of intermetallics occurs, see Figure 5. This microstructural change is probably given by the decomposition of $Al_9Mn_3Si$ needle-like intermetallics and formation of new rounded $Al_{19}Mn_4$ phase, which has very similar crystal structure as the $Al_9Mn_3Si$. However, the microstructure of the alloy remains very fine.

Long-term annealing tests of thermal stability showed that the hardness grows slightly after annealing for 100 h at 300 °C and after that it decreases to the same value as after 50 h and keeps constant (Figure 6). At 400 °C, this strengthening effect is negligible. This effect is probably connected with the decomposition of the supersaturated solid solution, producing precipitates of intermetallics. They then tend to coarsen and therefore the hardness decreases to a stabilized state. The changes in the phase composition are probably connected especially with the transformations between two structurally similar phases – $Al_9Mn_3Si$ and $Al_{19}Mn_4$, see Figure 7.

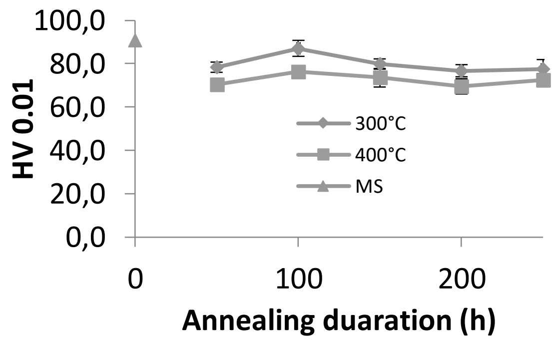


***Fig. 6*** *Microhardness (HV 0.01) vs. duration of annealing at 300 and 400 h*

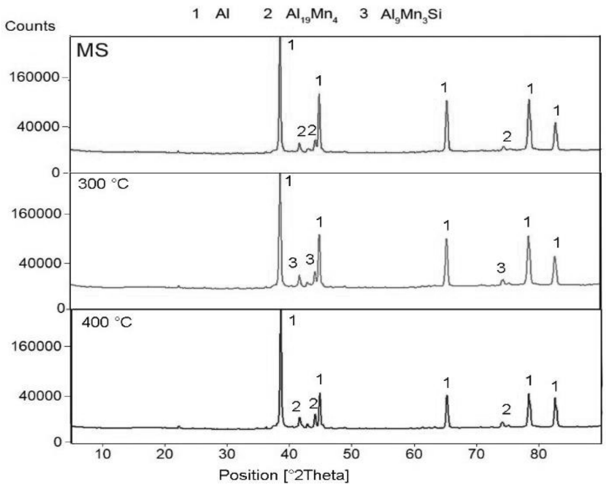


***Fig. 7*** *X-ray diffraction patterns of the rapidly solidified alloy before and after annealing at 300 and 400 °C for 250 h*

## 4 Conclusion

This paper is a part of the research dealing with non-conventional processing of deep-sea nodules. In this work, the nodules reduced by aluminothermic process were added to aluminium in the amount of 10 wt. %. The alloy was processed by gravity casting and by rapid solidification by the means of a melt spinning technology. The as-cast alloy contained aluminium-based solid solution, equilibrium phase $Al_6Mn$ with dissolved iron and the $Al_{19}Mn_4$ phase. After rapid solidification, only the solid solution and $Al_{19}Mn_4$ phase were detected by XRD. In reality, there are mainly needle-like particles of $Al_9Mn_3Si$, which is structurally similar to $Al_{19}Mn_4$ phase. Thermal exposure during thermal stability tests caused the needle-like $Al_9Mn_3Si$ to transform to nearly spherical $Al_{19}Mn_4$ phase. The hardness did not change significantly during long-term annealing at 300 and 400 °C for 250 h and therefore the alloy can be considered as thermally stable.

## Acknowledgement

***This research was supported by Czech Science Foundation, project No. 20-15217S.***

## References

[1] NOVAK, P., VU, N.H., SULCOVA, L., KOPECEK, J., LAUFEK, F., TSEPELEVA, A., DVORAK, P., MICHALCOVA, A. (2021). Structure and Properties of Alloys Obtained by Aluminothermic Reduction of Deep-Sea Nodules. In: *Materials*, Vol. 14, 561. MDPI. Switzerland. ISSN 1996-1944

[2] ŠVECOVÁ, I., TILLOVÁ, E., KUCHARIKOVÁ, L. (2017). Structural analysis of iron based intermetallic phases in secondary AlSi6Cu4 cast alloy, In: *Production Engineering Archives*, Vol. 15, pp. 3-6. De Gruyter, Poland. ISSN 2353-7779

[3] MACHUTA, J., NOVÁ, I., KEJZLAR, P. (2017). Structure and Mechanical Properties of Aluminium Alloys AlSi10 and AlSi5Mg. In: *Manufacturing Technology*, Vol. 17, pp. 772-777. UJEP. Czech Republic. ISSN 1213-2489

[4] LUŠTINEC, J., OČENÁŠEK, V. (2019). Residual Stresses and Cracks in Forgings of Heat-treatable Aluminium Alloys. In: *Manufacturing Technology*, Vol. 19, pp. 637-643. UJEP. Czech Republic. ISSN 1213-2489

[5] BOLIBRUCHOVÁ, D., BRŮNA, M. (2017). Impact of the Elements Affecting the Negative Iron-Based Phases Morphology in Aluminium Alloys - Summary Results. In: *Manufacturing Technology*, Vol. 17, pp.675-679. UJEP. Czech Republic. ISSN 1213-2489

[6] MOHAMED, M.J.S. (2015). Influence of Nickel Addition and Effect of Heat Treatment on Aluminium-Silicon Piston Alloys. In: *International Journal of Science and Research (IJSR),* Vol. 4, pp. 781 – 785. IJSR, India. ISSN 2319-7064

[7] PRŮŠA, F., VOJTĚCH, D., BERNATIKOVÁ, A., DVORSKÝ, D. (2015). Mechanical Alloying: A Way How to Improve Properties of Aluminium Alloys. In: *Manufacturing Technology*, Vol. 15, pp. 1036-1043. UJEP. Czech Republic. ISSN 1213-2489

[8] VOJTĚCH, D., BÁRTOVÁ, B., VERNER, J., ŠERÁK, J. (2004). Rychlé chlazení kovů – význa, technologie a využití. In: *Chemické Listy*, Vol. 98, pp. 180 – 184. ČSPCH, Czech Republic, ISSN 0009-2770