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Deep-sea nodules metallo-thermic reduction as a new "natural alloys" concept

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The expected growing consumption of color metal together with carbon emission restriction turns the eye to less frequent concept of metals production. Albeit the exploration of deep-sea nodules is not a new concept, we tried to find the way avoiding the high energy consumption for particular elements separation - reduce the ore in a single step without any separation process. Here the deep-sea nodules from Clarion-Clipperton franture zone (CCZ) in the Pacific Ocean are used. Obtained alloy can be then used as the additive for aluminum alloys.

The raw nodules are grinded and mixed with adequate amount of metallic powder. Ignited exothermic reaction produce metals´ mixture and some slag. The complicated and interesting part is the analysis of the metallothermic products, which contain plenty of phases and have complicated microstructure as process is quick and material contains many elements.

The highest attention was given to aluminothermic reduction, where wide variety of aluminum excess was explored. Equilibrium or zero excess value of reduction metal is calculated from amount of metallic cation in raw nodules and excesses up to 100 % were prepared and investigated, Fig. 1. All samples were investigated by X-ray diffraction (XRD) and the results were correlated with energy-dispersive spectroscopy (EDS) and electron back-scattered diffraction (EBSD) mapping in scanning electron microscope (SEM). XRD was measured in Bragg–Brentano geometry on a Bruker D8 Advance diffractometer and electron microscopy on SEM Tescan FERA 3 with analyzers Octane Super 60 mm^2 and DigiView V by EDAX, Ametek Inc. with all advanced options of provider.

As the CCZ nodules are predominantly manganese, even reduced metals contain mayor manganese rich phase, which develops from β-$Mn_{66}Ni_{20}Si_{14}$ phase ($P2_13$ space group) at 0 % of excess and β-Mn phase ($P4_132$ space group) at 10 % of excess to α-Mn phase (I-43m space group) at 20 % of aluminum excess. Samples contain up to 9 various phases, some of them – as MnS – with such small content that they were proved just by EDS/EBSD mapping. The Heusler phases Mn_2FeSi and Mn_2FeAl were observed as one of earliest observation within the presented projects [1]. Beyond structural observations the thermal stability up to 1600 °C, hardness, tribological properties and corrosion resistance were investigated [1, 2], even using reduced nodules in aluminum alloys [3]. The narrower set of alloys were reduced by titanium, Fig. 2.

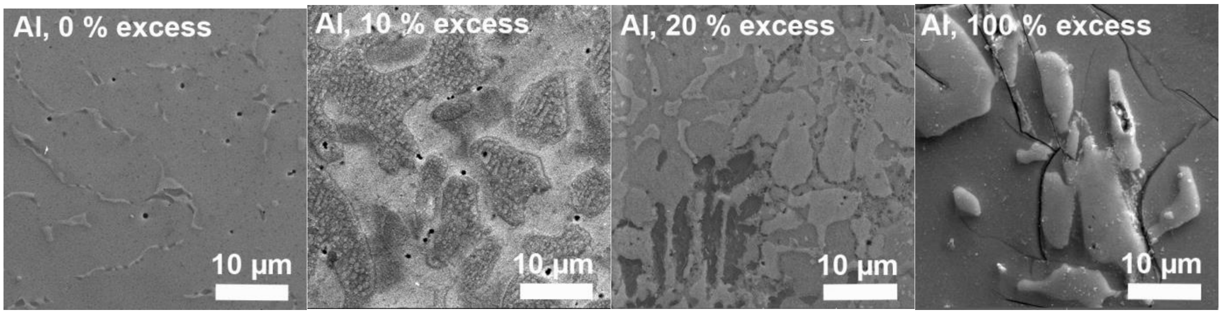

Figure 1. Metal after aluminothermic reduction with various excess of aluminum during reduction. Secondary electrons, polished surface.

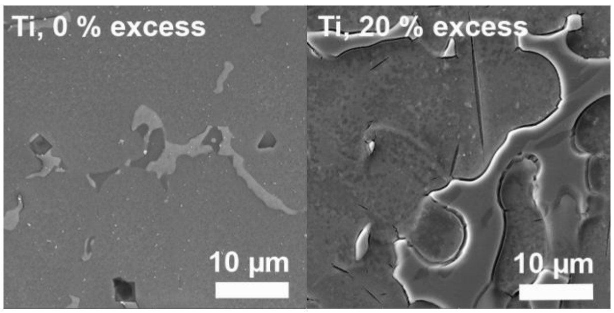

Figure 2. Metal after titanothermic reduction with various excess of aluminum during reduction. Secondary electrons, polished surface.

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