

PROCESSING OF DEEP-SEA NODULES AS A WAY TO NEW ALLOYS

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Abstract

Processing of polymetallic ores, especially deep-sea nodules, is always considered as extraction of individual metals. This work brings a new approach, i.e. to reduce the ore in a single step without any separation process. Such new metallurgical approach does not only save the costs, but also generates whole new alloys. The properties of these new alloys were tested. The applicability of the aluminothermic process, as well as the composition and possible use of the slag, are discussed. The alloys, containing manganese-based solid solution and intermetallics including the popular inverse Heusler phase $Mn_2Fe(Si,Al)$, are characterized by high hardness and wear resistance. Due to relatively low efficiency of the aluminothermic process, the aluminothermic slags contain significant amount of manganese and reasonable portion of nickel, copper and magnesium and therefore it could be still used as the raw material after the alloy was obtained by aluminothermy.

Keywords: Deep-sea nodules, manganese, alloy, aluminum alloy

1. INTRODUCTION

Deep-sea nodules (**Figure 1**), i.e. the polymetallic ores located on the seabed of oceans in the depth of several kilometres, have been considered for the last decades as the promising raw materials for extraction of various metals, such as manganese, cobalt and rare earth elements [1,2]. Considering that the earlier mentioned metals are considered as critical raw materials (CRM) by European Commission [3], the mining and processing of these ores could be of a high importance. However, both the mining technology and the metallurgical processing are costly and generates a lot of waste, when considering the extraction of individual elements from the nodules [4]. The currently available processing technologies include both pyro- and hydrometallurgical processes and their combinations [5-7].

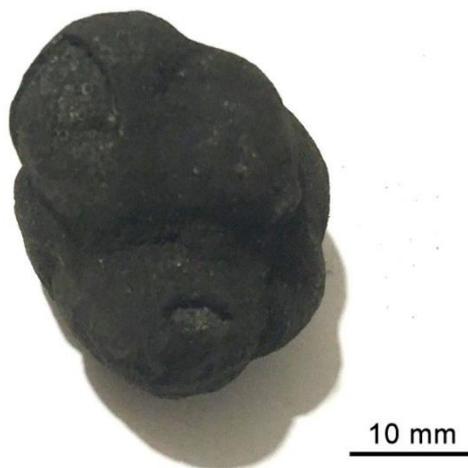


Figure 1 Manganese deep-sea nodule from Clarion-Clipperton Fracture Zone

This work brings a new approach – the processing of manganese-based deep-sea nodules complexly without the extraction of individual metals. As the reduction technology, aluminothermy was selected, because of its low energy demands and low carbon trace. The possible application of the obtained alloy is considered either as the alloy of manganese and also as the possible additive for aluminium.

2. EXPERIMENTAL PART

The deep-sea nodules, mined in the Clarion-Clipperton Fracture Zone in Pacific Ocean were initially characterized from the viewpoint of the chemical composition and also the internal microstructure. The chemical composition of the nodules was determined by X-ray diffraction (XRD). In order to observe the internal microstructure of the nodules, the nodule was cut and the metallographic sample was prepared of it by a standard metallographic procedure including grinding and polishing. The microstructure of the nodule was observed by optical (Nikon MA200) and scanning electron microscopy (SEM)-TESCAN VEGA 3LMU with Oxford Instruments X-max 20 mm² energy dispersive spectrometer (EDS). Before the aluminothermic reduction, the nodules were crushed to the powder. One half of the powder amount was annealed at 250 °C for 4 h for the release of the bonded water, while the other one was annealed at 500 °C for 4 h in order to change the oxidation state of manganese Mn₃O₄ in order to lower the reactivity of manganese. These two differently pre-processed powders were mixed and used in the aluminothermic process. Aluminum was used in stoichiometric amount calculated to allow the reduction of the oxides of Mn, Fe, Cu, Ni, Zn and Co, as could be expected on the basis of the Ellingham's diagram [8], as well as in the excess of 10 wt%. The aluminothermic reduction was carried out in a ceramic crucible of 85 mm in diameter, the batch of 250 g was tested. The aluminothermic reaction was initiated by the ignition mixture composed of aluminum powder, sodium peroxide and magnesium metal flakes [9].

The obtained alloys and slags were characterized from the viewpoints of chemical composition (X-ray fluorescence spectroscopy - XRF), microstructure, phase composition (X-ray diffraction – XRD - using PANalyticalX'Pert Pro diffractometer with Cu anode), Vickers hardness with the load of 10 kg (HV10) and wear resistance [9]. The efficiency of the aluminothermic reduction for the reduction of various included elements was considered.

3. RESULTS AND DISCUSSION

Before the reduction experiments, the chemical composition of the nodules and their internal structure were described. The nodule is composed of layers of metal-bearing compounds (oxides or hydroxides), forming concentric rings around the carbon-rich core. The core originates from the residues of organic origin, e.g. the shell of a prehistoric sea mollusc (**Figure 2**).

The pulverized nodules were analysed by XRD (**Table 1**) and reduced by the above-described aluminothermic process using two different levels of the aluminum amount – in the calculated stoichiometric amount (referred as “0 % Al”) and with the excess of 10 wt% (referred as “10 % Al”).

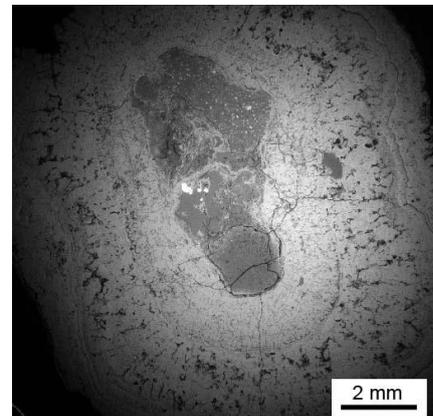


Figure 2 Microstructure of the deep-sea nodule

Table 1 Chemical composition of the deep-sea nodules, determined by XRF [9] (Only the elements with the concentration above 0.5 wt% are listed)

Element	Mn	Fe	Si	Al	Mg	Ca	Na	Cu	Ni	O
wt%	30.57	4.41	3.53	2.16	1.87	1.84	1.64	1.18	1.14	bal.

The results showed that the use of higher excess amount of aluminum in reduction increases the amount of the obtained alloy (**Table 2**). Regarding the chemical composition of the resulting alloys, the only significant difference was detected in the case of aluminum content. While the alloy reduced using the stoichiometric amount of aluminum contained less than 1 wt% of Al, the use of 10 % aluminum excess lead to the Al amount of approx. 7 wt% (**Table 3**).

Table 2 Weight of the alloys and aluminothermic slags after the reduction and their phase composition

	$m_{\text{alloy}}(\text{g})$	$m_{\text{slag}}(\text{g})$	phases - alloy	phases - slag
0 % Al	17.7	284.2	$\text{Mn}_{0.66}\text{Ni}_{0.2}\text{Si}_{0.14}$, $(\text{Cu},\text{Mn})_3(\text{Al},\text{Si})$, Mn_2P	$(\text{Fe},\text{Mn})\text{Al}_2\text{O}_4$, SiO_2 , $\text{NaAl}_{11}\text{O}_{17}$
10 % Al	22.5	284.6	$\beta\text{-Mn}$, Mn_2FeSi , Mn_2FeAl , Mn_2P	$(\text{Fe},\text{Mn})\text{Al}_2\text{O}_4$, SiO_2 , Al_2O_3

Phase composition of the alloys is listed in **Table 2**. The matrix of both alloys is composed of $\beta\text{-Mn}$ or the a structurally-relative multicomponent intermetallic phase ($\text{Mn}_{0.66}\text{Ni}_{0.2}\text{Si}_{0.14}$). The alloy reduced by the stoichiometric amount of aluminum contains also $(\text{Cu},\text{Mn})_3(\text{Al},\text{Si})$. Instead of this phase, the alloys prepared using the 10% excess of aluminum includes the $\text{Mn}_2\text{Fe}(\text{Si},\text{Al})$ inverse Heusler phase, which has been described just recently [10,11]. In addition to these phases, both of the alloys contain also manganese phosphide, which is located at the vicinity of the $(\text{Cu},\text{Mn})_3(\text{Al},\text{Si})$ or Heusler phases, see **Figure 3**, where the distribution and morphology of all present phases can be observed. The dark areas on the micrographs are pores and slag residues, which were not separated from the metal alloy sufficiently. The details about the identification of the phase composition by X-ray diffraction are listed in [9].

Table 3 Chemical composition of the alloys obtained by the aluminothermic reduction (XRF) and the slags

Element (wt%)	0 % Al - alloy	10 % Al - alloy	0 % - slag	10 % - slag
Mn	bal.	bal.	35.1	39.7
Al	0.9	6.9	37.7	38.0
Si	10.9	10.2	9.1	8.2
P	0.4	0.4		
Fe	18.2	17.3	2.1	2.3
Ni	4.8	4.8	0.4	0.4
Cu	4.6	4.7	0.4	0.4
Mg			3.8	5.0
Ca			3.5	3,4

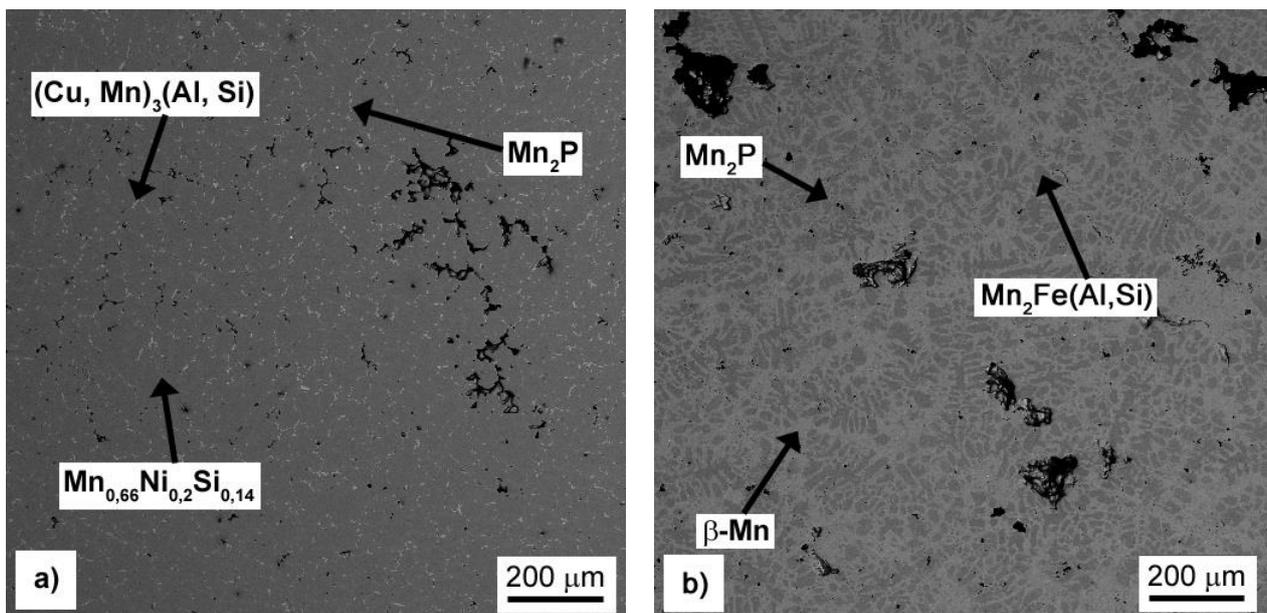


Figure 3 Microstructure of the alloys: a) 0 % Al, b) 10 wt% Al

The slags contain a spinel-type oxide - $(\text{Fe,Mn})\text{Al}_2\text{O}_4$ and silica (SiO_2). In addition to these phases, there was $\text{NaAl}_{11}\text{O}_{17}$ and Al_2O_3 detected in the case of alloy reduced using stoichiometric amount of aluminum and with the 10% excess, respectively (**Table 2**). The reason for the formation of aluminum oxide is the presence of residual unreacted aluminum in the slag, which has high affinity to oxygen. The slag contains significant amount of manganese and reasonable portion of nickel, copper and magnesium and therefore it could be still used as the raw material after the alloy was obtained by aluminothermy.

The mechanical, tribological and corrosion parameters of the alloys are listed in **Table 4**. It can be seen that the hardness of the alloys increases with the increasing amount of aluminum used for the reduction. The tribological parameters are rather unaffected by the increase of the aluminum content. However, the wear rate reaches the values typical for cold-work tool steels (e.g. AISI D2), but without the need of any heat treatment [9]. The values of friction coefficient also reach similar level as the tool steels or a bit higher. The values of polarization resistance increase with the growing amount of aluminum used for the reduction both in the tap water and model seawater. The higher is the polarization resistance, the lower is the corrosion rate in the particular environment, so it means that the corrosion rate lowers with increasing amount of aluminum used for the reduction. It is caused by the formation of a semi-protective layer of corrosion products (weak passivation layer) containing aluminum oxide on the surface [12].

Table 4 Hardness (HV_{10}), friction coefficient (f), wear rate (w) and polarization resistance (R_p) of the alloys [9,12]

Alloy	HV_{10}	$f(\text{Al}_2\text{O}_3)$ (-)	$w(\text{Al}_2\text{O}_3)$ ($\text{mm}^3/\text{N}\cdot\text{m}$)	$R_p(\Omega\cdot\text{m}^2)$ in tap water	$R_p(\Omega\cdot\text{m}^2)$ in model sea water
0 % Al	732	0.68	1.4×10^{-6}	0.416	0.470
10 wt% Al	790	0.68	1.9×10^{-6}	2.138	1.572

4. CONCLUSION

The aluminothermic reduction as the method for the processing of deep-sea nodules was evaluated. It was found the alloys have the chemical and phase composition strongly dependent on the applied amount of aluminium. The alloy reduced using the 10% excess of aluminum contained the inverse Heusler phase $\text{Mn}_2\text{Fe}(\text{Si,Al})$, while in the alloy obtained using the stoichiometric amount of aluminum there was low fraction of $(\text{Cu,Mn})_3(\text{Al,Si})$ phase instead. The slag after the reduction can be still considered as the raw material and processed further e.g. by hydrometallurgy. The alloys resulting from the aluminothermic process are characterized by very good wear resistance, comparable with cold-work tool steels, but without the need of any heat treatment.

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