MATERIALS
ENGINEERING

Magnesite-rich mining tailings as a raw material for refractory ceramics – microstructural and thermal analysis

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Abstract. In this paper, we present results of a study about the possibilities of utilizing talc ore mining tailings as a refractory raw material aiming at magnesium aluminate $MgAl_2O_4$ spinel composition. The mine tailings are rich in magnesite but contain also other minerals such as talc, chlorite, dolomite, and iron sulphides. As alumina source for spinel synthesis, we studied also another secondary raw material, an aluminium hydroxide precipitate, a by-product generated from the pickling process of aluminium anodizing. The goal of this paper is to study and compare a pure Mg–Al–O system and the corresponding Mg–Al–O system with some impurities. The formed phase and microstructures were examined by XRD, FESEM, and EDS studies. The thermal behaviour was studied using thermogravimetric analysis.

Key words: mining tailings, refractory ceramics, magnesium aluminate spinel, value from waste.

1. INTRODUCTION

Magnesium aluminate ($MgAl_2O_4$), spinel is the only intermediate compound in the phase diagram of the system $MgO–Al_2O_3$ [1]. It is an excellent refractory oxide having useful physical, chemical, and thermal properties: a high melting point (2135 °C), excellent resistance against chemical attack, and very good thermal characteristics both at ambient and elevated temperatures. Due to these desirable properties, $MgAl_2O_4$ spinel has a wide range of applications in the structural, chemical, optical, and electrical industries [2,3]. As a refractory material, $MgAl_2O_4$ spinel has applications in the form of sintered ceramics or coatings, e.g. for surfacing furnace parts. In particular, porous $MgAl_2O_4$ spinel ceramic is used as a thermally insulating material at high temperatures for the steel-making industry [4]. Due to

its high melting point and high chemical inertness, $MgAl_2O_4$ spinel has also been used to replace traditional chromite-based refractories in cement rotary kilns and steel ladles [5].

Calcination of magnesite ($MgCO_3$) is the principal route by which magnesia (MgO) is formed for the use as a refractory ceramic raw material [6]. In Europe, magnesite is extremely scarce and in high demand, thus it was included in the 2014 EU 'Critical Raw Materials' list [7]. China, North Korea, and Russia account for 65% of the global magnesite reserves with China being the largest magnesite producer [8]. In the path towards resource efficiency, mining tailings are a key resource to take advantage of considering their large volumes, environmental impact, and the need for the efficient exploitation of natural resources [9].

In this paper, we discuss possibilities of utilizing mine tailings from talc ore mining as a refractory raw material aiming at magnesium aluminate ($MgAl_2O_4$)

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spinel composition. The main goal of the research was to examine the possibility of utilizing mining tailings containing impurities as low-cost, but presumably non-ideal, raw materials in an effective way. Mine tailings from talc ore mines are rich in magnesite (70–80%). Other minerals are 10–15% talc, 5–10% chlorite, 2–10% dolomite, and 0.5–1% iron sulphides [10]. As the alumina source for spinel synthesis, we used another secondary raw material, an aluminium hydroxide precipitate, a by-product generated from the pickling process of aluminium anodizing. As a reference, a stoichiometric $MgAl_2O_4$ spinel was synthesized by using commercially available MgO and AlO(OH) powders. The goal was to compare a pure Mg–Al–O system and an analogous Mg–Al–O system with some impurities (Si^{4+}, Fe^{3+} cations) present. The formed phase and microstructures were examined by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and energy dispersive spectroscopy (EDS) studies. The ultimate aim of the research was to examine the possibility of utilizing impurity containing mining tailings as economical but presumably non-ideal raw materials in an effective way.

2. EXPERIMENTAL PROCEDURE

2.1. Raw materials

The raw materials selected for the investigation were mining tailings from a talc ore mine and aluminium hydroxide precipitate, a by-product generated from the pickling process of aluminium anodizing. The mining tailings sample was taken from one point of a temporary storage pile; therefore, it is not necessarily representative of the whole mining tailings area of its origin as the mineralogy, grain size, and chemistry of tailings may vary in different parts of the deposit. Table 1 shows the mineralogical composition of the talc ore tailings. Mineralogical characterization included the identification and quantification of mineral phases with scanning electron microscopy (SEM) together with elemental analyses. Table 2 presents the total concentrations of cations (calculated as oxides) in the tailings sample, measured with X-ray fluorescence spectrometry (XRF).

Table 1. Main identified minerals in the talc ore tailings sample (% of total volume)

Mineral	Content, vol%
Magnesite, $MgCO_3$	80.4
Talc, $Mg_3Si_4O_{10}(OH)_2$	9.4
Chlorite, $(Mg,Fe)_5Al(Si_3Al)O_{10}(OH)_8$	4.9
Dolomite, $CaMg(CO_3)_2$	1.8

Table 2. Chemical composition of the talc ore tailings sample as revealed by XRF

	MgO	SiO_2	Fe_2O_3	Al_2O_3
Tailings content, %	38.5	10.1	8.16	0.61

The more detailed explanation of the mineralogical analyses, geochemical analyses, and sampling procedure are presented in [11].

As the alumina source, aluminium hydroxide precipitate, a by-product generated from the pickling process of aluminium anodizing, consisting mainly of gibbsite (aluminium oxide trihydrate, $Al(OH)_3$) with traces of Na_2SO_4, was used. As a reference, pure magnesium aluminate $MgAl_2O_4$ spinel was prepared using commercially available powders of MgO and boehmite (aluminium oxide hydroxide, AlO(OH)), average grain size < 0.77 μm. The MgO powder was provided by Inframat and the boehmite powder, by Sasol Germany GmbH.

2.2. Synthesis experiments

Experimental powder mixtures were prepared aiming at magnesium aluminate ($MgAl_2O_4$) spinel composition. Recipes shown in Table 3 were formulated with 1 : 2 Mg to Al molar ratio. The talc ore tailings were received in powder form, but the powder was first ground by jet milling into the particle size below 10 μm in order to increase its reactivity and ensure a good mixing of the ingredients. Ceramic powder suspensions (water-based) were prepared from raw material mixtures by bead milling for 15 min. Suspensions were dried with an industrial scale spray dryer Niro Atomizer to produce agglomerated powders. Agglomerated powders were uniaxially compressed into green pellets of 20 mm × 3 mm using approximately 25 MPa pressure. Green state pellets were heat treated in an ENTECH air chamber furnace in ambient air atmosphere and pressure. The powders were heat treated at six different temperatures: 1000, 1100, 1200, 1300, 1400, and 1500 °C. The heating rate was 3.3 °C/min up to the maximum temperature. After 3 hours of holding time, the mixtures were cooled to room temperature at the rate of 5 °C/min.

Table 3. Test matrix recipes for the spinel experiments (wt%)

| Recipe code	MgO	AlO (OH)	Talc ore tailings	Aluminium hydroxide precipitate
Recipe1	25.1	74.9	0	0
Recipe2	0	0	35	65

2.3. Characterization methods

The thermal behaviour of agglomerated powders was studied using thermogravimetric analysis (TG, Netzsch STA449 F1 Jupiter) giving a simultaneous differential scanning calorimetry (DSC) signal. The tests were conducted in air atmosphere in a temperature range from 40 to 1500 °C with the heating rate of 10 °C/min. The phase structure was analysed for agglomerated powders and heat-treated pellets by using an X-ray diffractometer (XRD, Empyrean, PANalytical B.V., ALMELO, Netherlands) with a CuKα radiation source, and analysed using HighScore Plus software with ICDD database. The XRD was operated at 45 kV and 40 mA with a scanning rate of 3° 2θ/min. Compressed pellets were characterized after heat treatments.

For microstructural analyses, metallographic cross-sections were prepared by casting cut sections of specimens in Epofix cold setting resin under reduced pressure. The casts were then ground, polished, and carbon coated for electrical conductivity. Microstructural and compositional investigations of the materials were conducted with FESEM (Zeiss ULTRAplus microscope) and EDS and operating on a Noran NSS software. The polished cross-sections were studied by SEM using an angle-selective backscattered electron (AsB) detector in order to maximize the compositional contrast.

3. RESULTS AND DISCUSSION

3.1. Agglomerated powders

The TG and DSC curves of agglomerated powders for the two recipes are presented in Fig. 1. For Recipe1 powder (Fig. 1a), the DSC curve showed an endothermic peak centred at 382 °C and accounting for approximately 12% of the initial weight loss in the TG curve. This was probably caused by the dehydration of magnesium hydroxide, which was formed by the reaction with the spray drying water. Prior to that transformation, evaporation of water occurred (below 290 °C). The second endothermic peak, at 504 °C in the DSC curve, accounted for approximately 10% of the weight loss in the TG curve and was attributed to boehmite dehydraoxylation. The exothermic peak at 1012 °C was most probably related to the spinel crystallization. No weight change was related to this phase transformation. For Recipe2 (Fig. 1b), approximately 36% weight loss was observed already below 600 °C, most likely due to the decomposition of $Al(OH)_3$ and $MgCO_3$. The peak at 853 °C is related to the weight loss of approximately 7%; this finding could be connected to the decomposing of talc. The DSC curve showed also transformation above 1200 °C, with no accompanying weight change in the
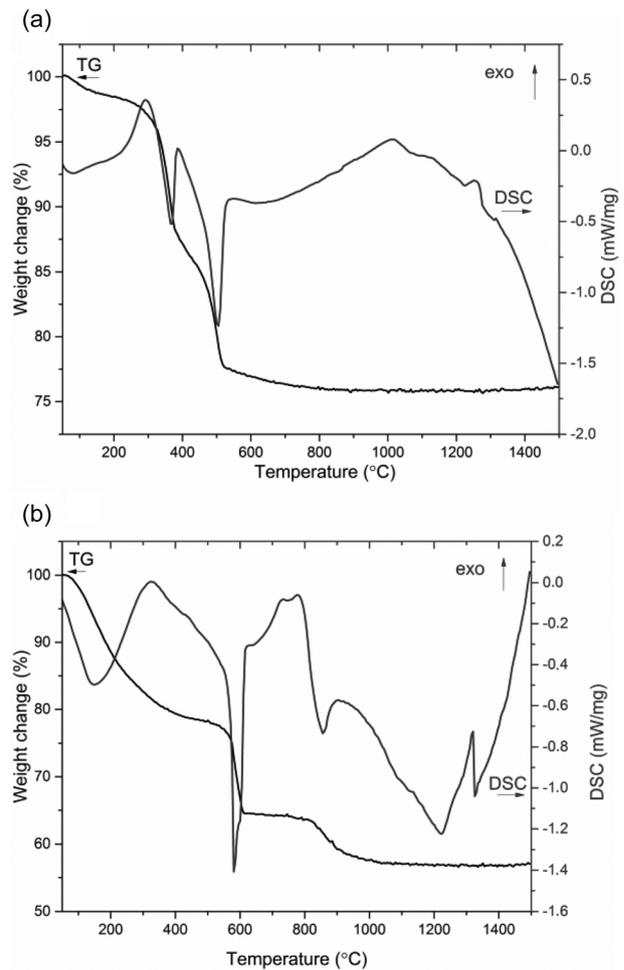

Fig. 1. Thermogravimetric (TG) and differential scanning calorimetry (DSC) curves for agglomerated powders: (a) Recipe1 and (b) Recipe2.

TG curve. Thus, above 1200 °C the peaks can most likely be attributed to the solid–solid phase transformations.

3.2. Sintered pellets

Figure 2 illustrates the phase structure evolution for compressed pellets of both recipes after heat treatments at 1000–1500 °C. For Recipe1 pellets, the $MgAl_2O_4$ spinel phase was the only crystalline phase at all temperatures. The only difference between the applied six temperatures was the peaks widths, indicating that the crystal size increased with the increasing temperature. For Recipe2 compressed pellets, the $MgAl_2O_4$ spinel phase was the main crystalline phase at all temperatures, but also minor peaks related to the ferran forsterite phase, $(Mg, Fe)_2SiO_4$, were detected at all temperatures. The peaks of forsterite were of lower intensity at higher temperatures. Peak widths, indicating the crystal size,
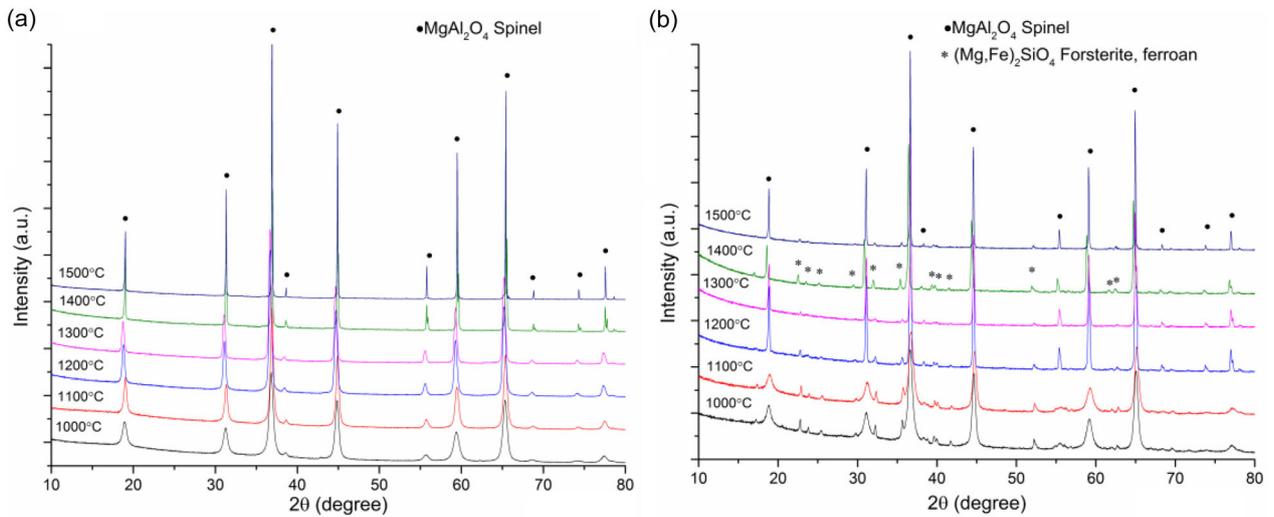
Fig. 2. XRD patterns for powder pellets heat treated at different temperatures: (a) Recipe1 and (b) Recipe2.

were smaller at high temperatures. Additionally, the XRD spectra related to heat-treated pellets of Recipe2 showed a slight increase in the overall intensity of the curve at low 2θ values; thus the presence of an amorphous phase was possible.

Figure 3 shows FESEM images of pellets treated at 1300 °C. Recipe1 produced a very fine structure of $MgAl_2O_4$ spinel crystals. Recipe2 introduced $MgAl_2O_4$ spinel crystals surrounded by an amorphous phase, seen in darker grey than the spinel phase. Also another crystalline
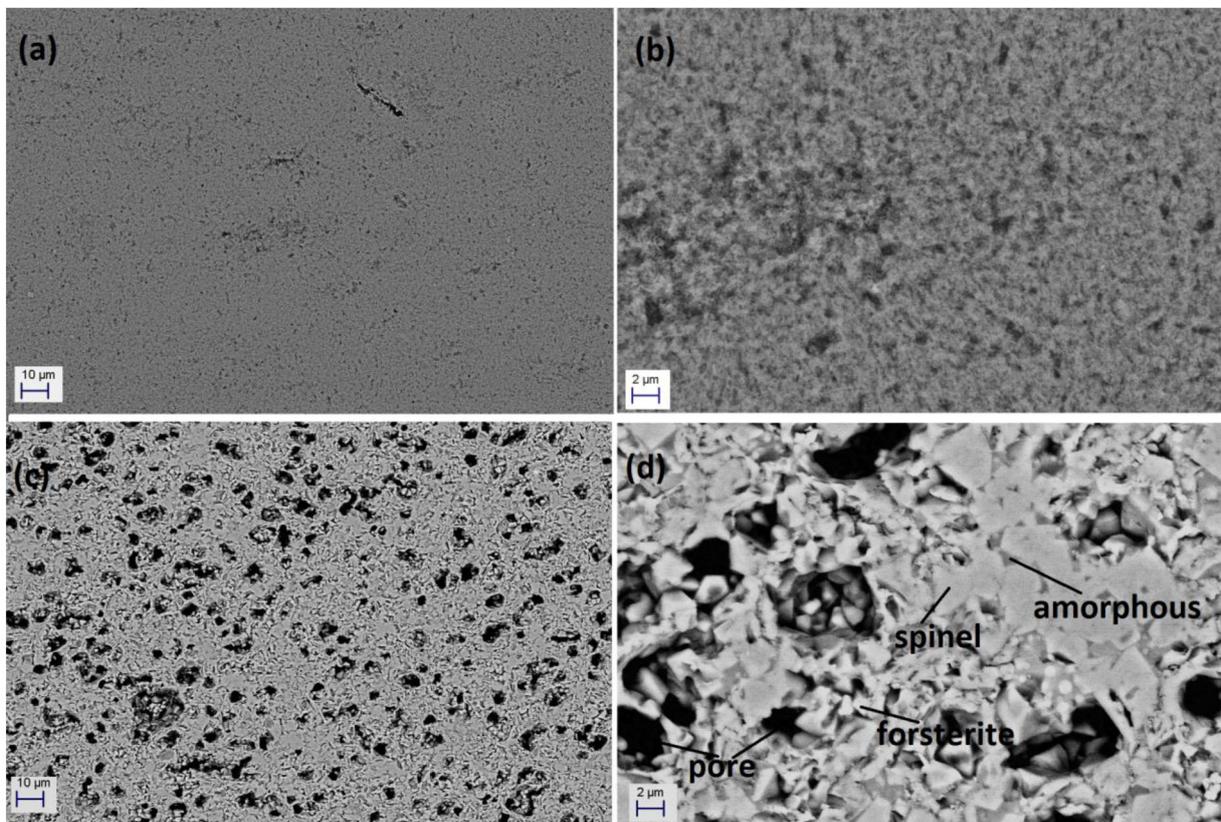
Fig. 3. FESEM images of cross-sections of pellets treated at 1300 °C (a,b) Recipe1 and (c,d) Recipe2.

phase was observed in areas with a bright contrast, most likely it was the ferron forsterite, $(Mg, Fe)_2SiO_4$, phase. According to EDS analyses, it is challenging to draw any definite conclusion about the compositional details, due to their microstructural complexity and fine crystal size compared to the electron beam size. Nevertheless, these characterization results suggest that Fe^{3+} cations were concentrated on crystal phases, most likely to the ferron forsterite, $(Mg, Fe)_2SiO_4$, phase. Partly Si^{4+} cations were also included in the forsterite phase and partly in the amorphous phase. Porosity, seen in black contrast, was also present in both samples, particularly in Recipe2. The more porous structure in Recipe2 pellets evolved due to a relatively higher fraction of evaporating phases (inducing weight losses) consistent with observations on TG/DSC curves (Fig. 1).

4. CONCLUSIONS

The results from this research suggest that synthesis of magnesium aluminate $MgAl_2O_4$ spinel is possible using secondary raw material sources, such as mining tailings from talc ore mining and a by-product from the aluminium anodizing process. Mine tailings from a talc ore mine are rich in magnesite but contain also other minerals such as talc, chlorite, dolomite, and iron sulphides. According to the results, both Si^{4+} and Fe^{3+} cations could be included in the crystalline forsterite phase. Additionally, presence of Si^{4+} cations induced the formation of an amorphous phase. Future work will concentrate on a more detailed characterization of the properties of the secondary raw material-based spinel ceramics.

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REFERENCES

1. Dal Maschio, R., Fabbri, B., and Fiori, C. Industrial applications of refractories containing magnesium aluminate spinel. *Ind. Ceram.*, 1988, **8**(3), 121–126.
2. Li, H., Wei, H-Y., Cui, Y., Sang, R-L., Bu, J-L., Wei, Y-N., et al. Synthesis and characterisation of $MgAl_2O_4$ spinel nanopowders via nonhydrolytic sol–gel route. *J. Ceram. Soc. Jpn.*, 2017, **125**(3), 100–104.
3. Yan, W., Lin, X., Chen, J., Li, N., Wei, Y., and Han, B. Effect of TiO_2 addition on microstructure and strength of porous spinel ($MgAl_2O_4$) ceramics prepared from magnesite and $Al(OH)_3$. *J. Alloys Compd.*, 2015, **618**, 287–291.
4. Ganesh, I. Fabrication of magnesium aluminate ($MgAl_2O_4$) spinel foams. *Ceram. Int.*, 2011, **37**, 2237–2245.
5. Ganesh, I. A review on magnesium aluminate ($MgAl_2O_4$) spinel: synthesis, processing and applications. *Int. Mater. Rev.*, 2013, **58**(2), 63–112.
6. Walling, S. A. and Provis, J. L. Magnesia-based cements: a journey of 150 years, and cements for the future? *Chem. Rev.*, 2016, **116**, 4170−4204.
7. *Report on Critical Raw Materials for the EU: Report of the Ad Hoc Working Group on Defining Critical Raw Materials*. European Commission, Brussels, Belgium, 2014.
8. Magnesium compounds. In *Mineral Commodity Summaries 2015*. U.S. Geological Survey, Reston, VA, 2015, 96−97.
9. Lottermoser, B. G. Recycling, reuse and rehabilitation of mine wastes. *Elements*, 2011, **7**, 405–410.
10. Räisänen, M-L. *Magnesiittirikastushiekan ympäristökelpoisuus*. Report Dnro K43/41/02. Geological Survey of Finland, 2004 (in Finnish).
11. Solismaa, A., Ismailov, M., Karhu, H., Sreenivasan, M., Lehtonen, P., Kinnunen, M., et al. Valorization of Finnish mining tailings for the use of ceramic industry. *Bull. Geol. Soc. Finl.*, 2018, **90**, 33–54.

Magnesiidirikka kaevandusjäätme kui rasksulava keraamika tooraine kasutamine – mikrostruktuuri- ja termoanalüüs

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On uuritud talgimaagi kaevandusjäätmete kasutamise võimalusi toorainena magneesiumaluminaadi valmistamiseks. Kaevandusjääde on magnesiidirikas, kuid sisaldab ka teisi materjale, nagu talk, kloriit, dolomiit ja raudsulfiid. Alumiiniumoksiidi allikana uuriti ka teisest tooret alumiiniumhüdroksiidi kui sadestist alumiiniumi anodeerimise kaasproduktina. Töö eesmärgiks on uurida ja võrrelda puhast Mg-Al-O ning mõningaid lisandeid sisaldavaid Mg-Al-O süsteeme. Moodustunud faase ja mikrostruktuure uuriti XRD-, FESEM- ning EDS-meetodiga. Termilist käitumist uuriti termograafilise analüüsi meetodit kasutades. Uuriti lisandeid sisaldavate kaevandusjäätmete kasutamist kui ökonoomset, kuid eeldatavalt mitteideaalset toorainet efektiivsel teel. Töö tulemusena selgitati, et magneesium-aluminaadi $MgAl_2O_4$ süntees on võimalik, kasutades teisese toorme ressursse.