The Effect Of Spinel Addition On The Mechanical Behaviours Of MgO-Hercynite Refractories

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***Abstract*— In this work, the incorporation of spinel particles ($MgAl_2O_4$) into MgO-hercynite ($FeAl_2O_4$) at different ratios has been examined to improve mechanical properties of MgO-hercynite composite refractories. The relationships between mechanical properties and microstructural variables have been investigated in detail. The important parameters improving the mechanical properties of MgO-hercynite-spinel composite refractory materials have been determined. 1.5 times improvement of the fracture toughness and fracture surface energy values have been achieved compared to M-%5H material. Also, M-%10H-%5S material has had ~ 2 times bigger work of fracture than M-%5H material.**

***Keywords*— MgO, hercynite, $FeAl_2O_4$, spinel, $MgAl_2O_4$, composite, refractories, mechanical properties, density**

I. INTRODUCTION (*Heading 1*)

Refractory materials can withstand high temperatures, maintain its physical and chemical properties in the atmosphere at high temperatures [1].

Chromium-free refractory bricks are produced and preferred in the last 20 years in order to solve the environmental pollution caused by use of the magnesia-chrome brick in cement kiln [2].

In recent years the production of MgO-spinel bricks and MgO-hercynite bricks as alternatives to MgO-chrome brick have become widespread [3].

Magnesium aluminate spinel ($MgAl_2O_4$) is an important component of magnesia based refractories. $MgAl_2O_4$ is not a natural material, is formed by the reaction between magnesium and aluminum oxide The melting temperature of $MgAl_2O_4$ is 2135 °C [4, 5].

In general, commercially hercynite production is carried out by solid state reactions of oxides at elevated temperatures and longer time (such as 16 hours), under very low oxygen pressure / controlled atmosphere [6].

MgO–spinel bricks are preferred in the cooling and transition zones where thermal stresses occur due to high temperature difference and therefore severe thermal shocks taking place during cooling and heating in cement rotary kilns [7].

Magnesia-hercynite bricks have better coatability than magnesia-spinel bricks. Also have better thermal shock resistance, good corrosion resistance as magnesia-spinel bricks [8].

In this study, the mechanical properties, fracture toughness and therefore the service life MgO-hercynite composite refractories were intended to be improved by spinel addition. The relationships between the mechanisms causing improvements in the mechanical behaviours of composite refractories and microstructure and parameters affecting these were examined.

II. MATERIAL AND METHOD

A. *Material Preparation*

Recipes were prepared by incorparating respectively weights of 5%, 10% and 20% $MgAl_2O_4$ spinel (S) to the compositions obtained by additions of 5%, 10% and 20% hercynite (H) by weight to MgO (M). Those recipes were shaped as ~230x115x65 mm^3 dimensions by applying ~127.5 MPa (300 bar) press pressure. Then, sintered nearly 1550 °C temperature.

B. *Density Measurement*

Three parts were cut for each materials prepared in different compositions, these pieces were boiled into water for 2 hours and cooled to room temperature. Then, density and open porosity values were determined by Archimedes principles.

C. *Mechanical Testing*

The materials were cut into 2.5 cm × 2.5 cm × 15 cm bar according to the standards. The strength(σ) and elastic modulus (E) were determined by the 3-point bending method in Instron 5581 [9, 10].

The fracture toughness, fracture surface energy (γ_i) and work of fracture (γ_{WOF}) values of the samples, is calculated with the Single Edge Notching (SENB) method by Instron 5581. Notch depth was measured by Olympus brand BX60M optical microscope (magnification: 50x) [11-15].

D. Microstructure Analysis

SEM (scanning electron microscope) studies carried out with Zeiss Evo 50 device, microstructure and fracture surfaces of the materials were investigated. The mean MgO grain size was calculated by a standard line mean intercept method [16], using SEM pictures taken on the polished and thermally etched surface of the specimen.

III. RESULTS AND DISCUSSION

A. Density

The mechanical tests of MgO-hercynite-spinel composite materials, prepared by incorparating respectively weights of 5%, 10% and 20% $MgAl_2O_4$ spinel (S) to the compositions obtained by additions of 5%, 10% and 20% hercynite (H) by weight to MgO (M), were conducted. The results of the density and open pores are given in Figure 1-2.

Densities of all material compositions decrased as the value of open porosity was increased. In general, density values of MgO-hercynite-spinel (M-H-S) composite refractory materials were lower than the MgO-hercynite materials. The maksimum density values were achieved in M-5H%-5S% and M-%5H-%10S refractories.

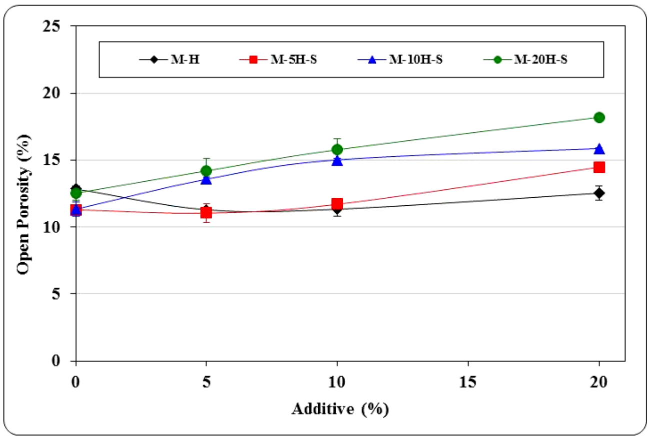

Fig. 1. *Open porosity values of MgO-hercynite-spinel Composite Refractoies.*

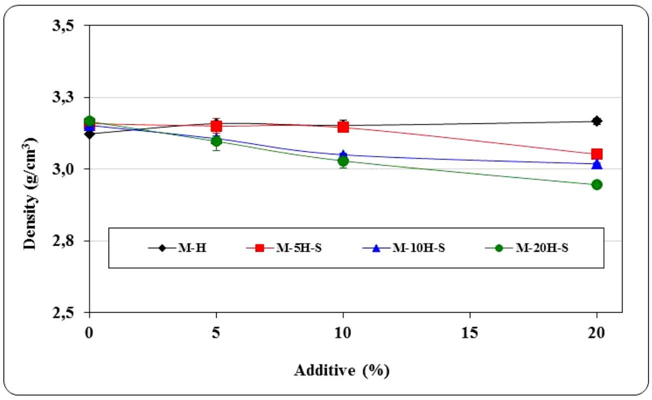

Fig. 2. *Density values of MgO-hercynite-spinel Composite Refractoies.*

B. Mechanical Behaviours

The strength and elastic modulus values of MgO-hercynite (M-A-H) composite refractory materials were lower than the MgO material. Also those values were reduced by adding increasing hercynite.

During cooling after sintering, significant amount of tensile stresses were formed around hercynite grains due to the large differences between thermal expansion coefficients (α) of MgO and hercynite (between 25–1000 °C: α_{MgO}=13.6 x 10^{-6} °C^{-1}, $\alpha_{Hersinit}$=9.0 x 10^{-6} °C^{-1}). And those stresses led to the formation of microcracks in the form of networks connected to each other. Therefore MgO-hercynite composites had low strength and elastic modulus (Figure 3, 4).

Strength and elastic modulus values of MgO-hercynite-spinel composite refractory materials were close to each other and lower than pure MgO-hercynite (M-H) refractory materials. The strength and elastic modulus decreased with the increase amount of hercynite (Figure 3, 4). The reason for the decrease in strength and elastic modulus were probably microcracks caused by differences in thermal expansion coefficients of MgO-hercynite–spinel (between 25–1000 °C: α_{Spinel} = 8.4 x 10^{-6} °C^{-1}).

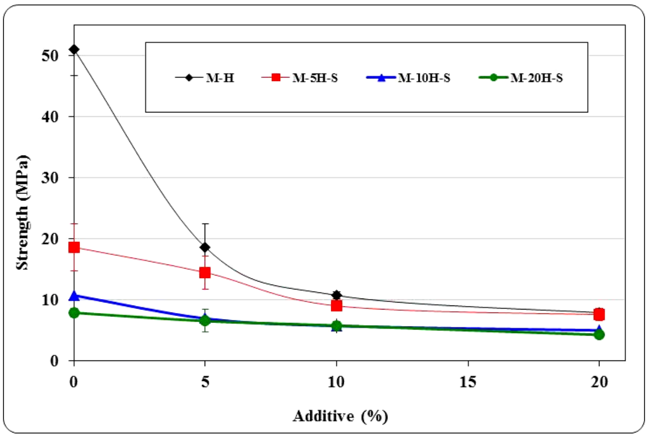

Fig. 3. *Strength values of MgO-hercynite-spinel Composite Refractoies.*

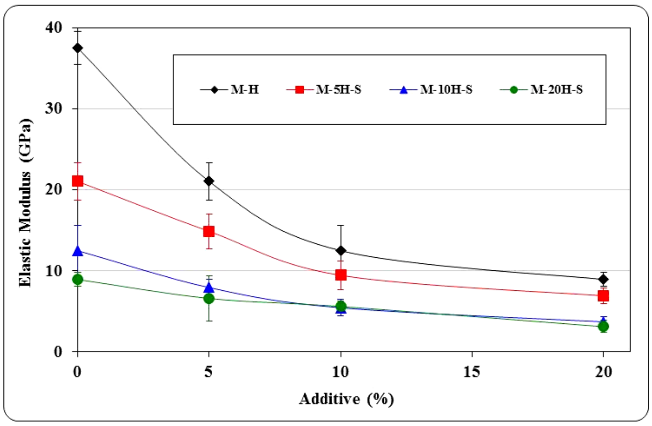

Fig. 4. *Elastic Modulus values of MgO-hercynite-spinel Composite Refractoies.*

In general, MgO-hercynite composite materials had lower fracture toughness than MgO material (Figure 5). In other words, the resistance to fracture of MgO decreased with the addition of hercynite. Also, the fracture surface energy values of MgO-hercynite composite refractory materials were lower than MgO (Figure 6).

The fracture toughness values of MgO-hercynite-spinel (except M-5H%-5S%) were lower than MgO-hercynite refractory materials (Figure 5). Also, MgO-hercynite-spinel composite refractory materials except M-%5H had lower fracture surface energy than MgO-hercynite refractories (Figure 6). Fracture toughness and fracture surface energy values decreased as a function of hercynite amount.

Approximately 1.5-fold improvement in fracture toughness and fracture surface energy values of M-5H%-5S% material than M-%5H material was observed (Figure 5, 6).

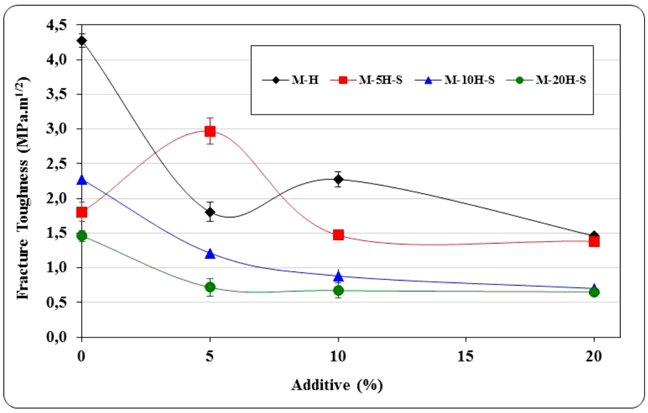

Fig. 5. *Fracture Toughness values of MgO-hercynite-spinel Composite Refractoies.*

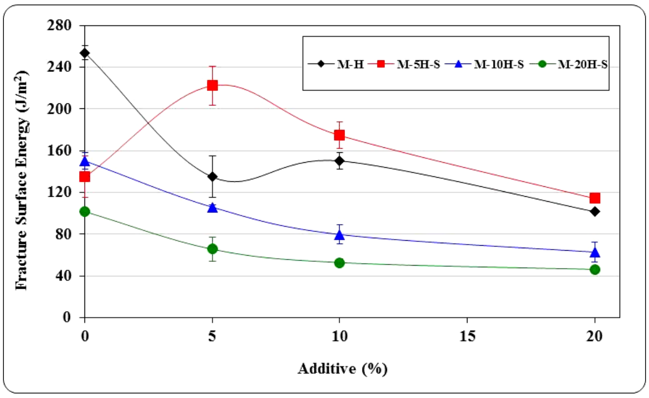

Fig. 6. *Fracture surface energy values of MgO-hercynite-spinel Composite Refractoies.*

In general, the work of fracture values required for fracture all materials increased as the amount of hercynite increased. Microcracks formed due to the differences in thermal expansion coefficient helped to alleviate the stress caused during the heating process in service use and easily cause hindrance to the progress of the new micro-cracks formations. For those reasons, work of fracture values of composite materials including hercynite were higher than pure MgO (Figure 7).

Overall the results, the work of fracture values of MgO-hercynite-spinel composite refractory materials were higher than pure MgO-hercynite material with low additive amounts (5 %, 10%), but generally, the work of fracture values of MgO-hercynite-spinel became lower with increasing amount of hercynite. Approximately 2-fold improvement in work of fracture value of M-10H%-S%5 material was achieved than M-5H% material (Figure 7).

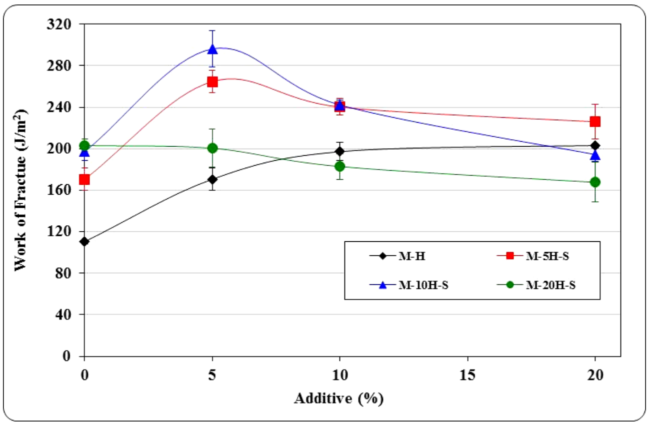

Fig. 7. *Work of fracture values of MgO-hercynite-spinel Composite Refractoies.*

C. Electron Microscope Characterizaton

The image of the microstructure of 3-4% iron-containing MgO material produced in factory conditions is given Figure 8. Average grain size of MgO was calculated as 66.251 μm.

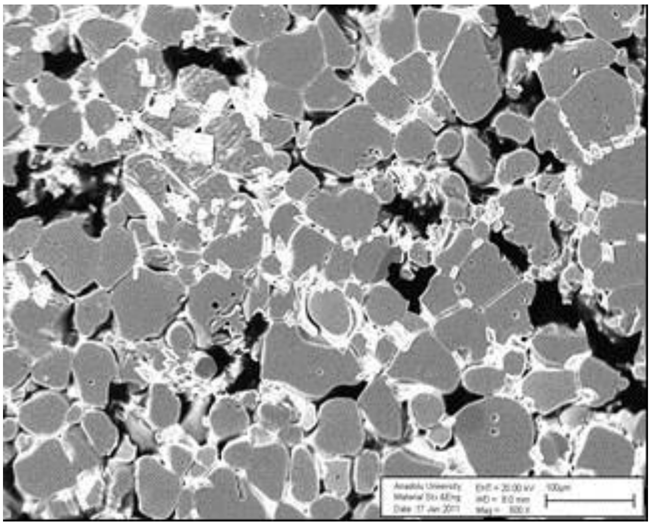

Fig. 8. *The image of the microstructure of iron-containing MgO material (magnification: 500x).*

Some part of black region observed showed pores formed in the structure, another part of black region was considered to be caused by leaving grains during the polishing process (Figure 8). The liquid phase formation in MgO material was low, white region observed in grain boundaries were monticellite phase.

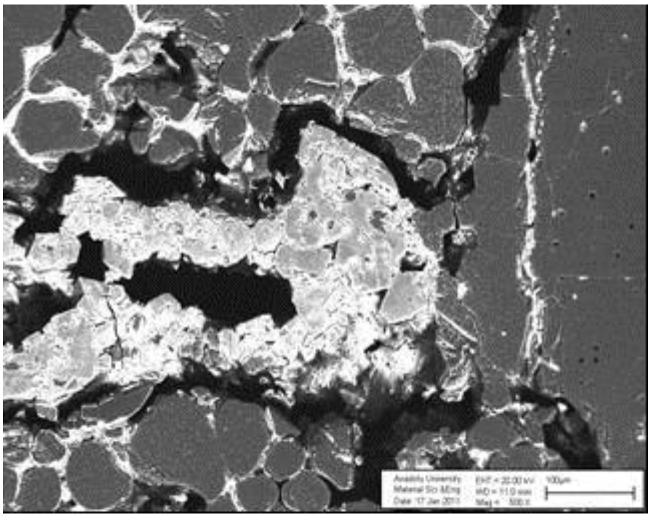

Fig. 9. *The image of the microstructure of M-10H% material (magnification: 500x).*

In MgO-hercynite produced by adding hercynite; the holes between the ferrous-MgO and hercynite grains, cracks in MgO and hercynite grains (transgranular cracks) and in the grain boundaries (intergranular cracks) were observed (Figure 9). Average grain size of MgO was calculated as 57.35 µm.

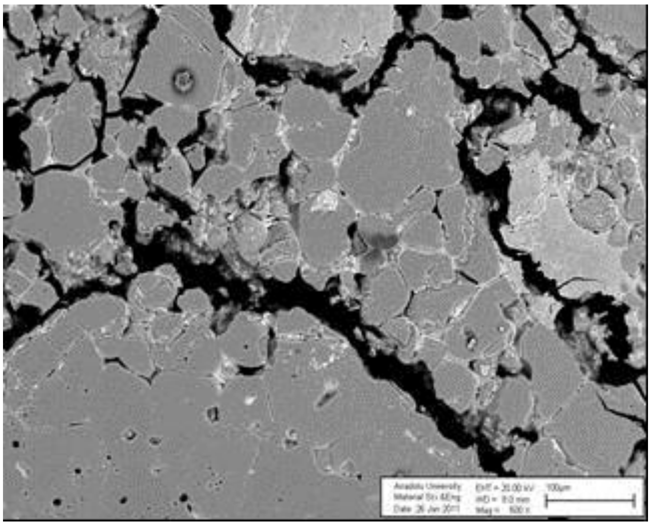

Fig. 10. *The image of the microstructure of M-10H%-5S% material (magnification: 500x).*

When examining the microstructure images of MgO-10hersinit%-5spinel% (M-10H%-5S%)composite refractory material, non homogeneous distribution of the used compounds were observed. In general, big holes between MgO and hercynite grains, cracks in MgO grains and intergranular cracks were observed, also. Those cracks were stopped when it reached the hercynite grains (Figure 10). The average crystal size of MgO was calculated as 50.128 µm in the M-10H% MgO% material.

The fracture surface image of iron containing-MgO refractory material is given in Figure 11.

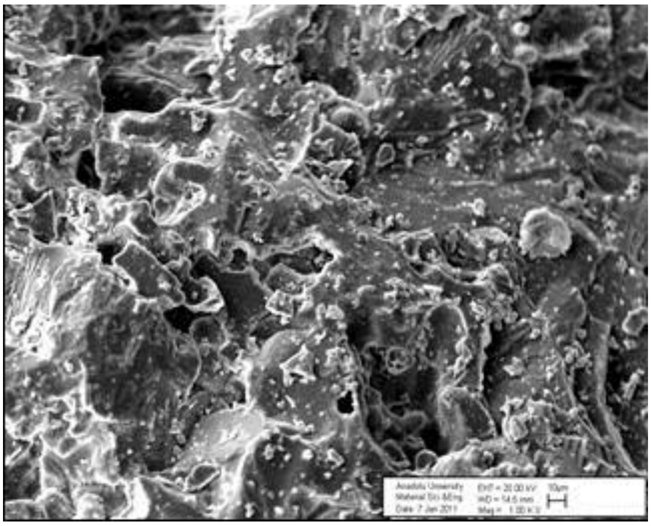

Fig. 11. *The fracture surface image of iron-containing MgO material.*

In general, the pure iron-containing MgO material was exposed to transgranular cracks. In particular, the cracks of medium-large-sized crystal grains were transgranular cracks type predominately. Due to this type of crack character, the material had relatively high resistance against the crack beginning, but the resistance to crack propogation was low.

The fracture surface image of the refractory composite material formed by addition of 10% hercynite to iron-containing MgO is given in Figure 12.

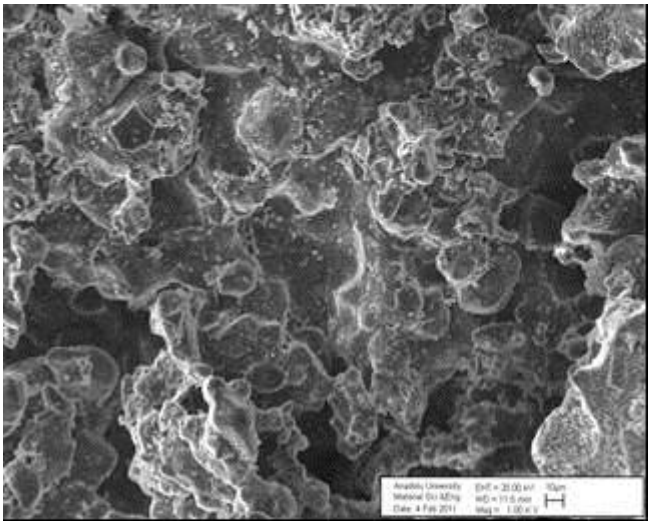

Fig. 12. *The fracture surface image of M-10H% refractory material.*

Large tensile stresses and microcracks were occurred in the structure due to thermal expansion coefficient differences between the MgO and hercynite grains during cooling after the sintering of composite materials.

Microcracks in the material were connected to each other, stopped when they hercynite grains or changed their direction during the breaking of material. According to fracture surface image of

MgO-hercynite material, either transgranular cracks or intergranular cracks were observed (Figure 12).

The fracture surface image of MgO-10hercynite%-5spinel% refractory material is given in Figure 13. According to the image, either transgranular cracks or intergranular cracks were occurred, transgranular cracks were predominant in coarse grains and also intergranular cracks were predominant for smaller grains.

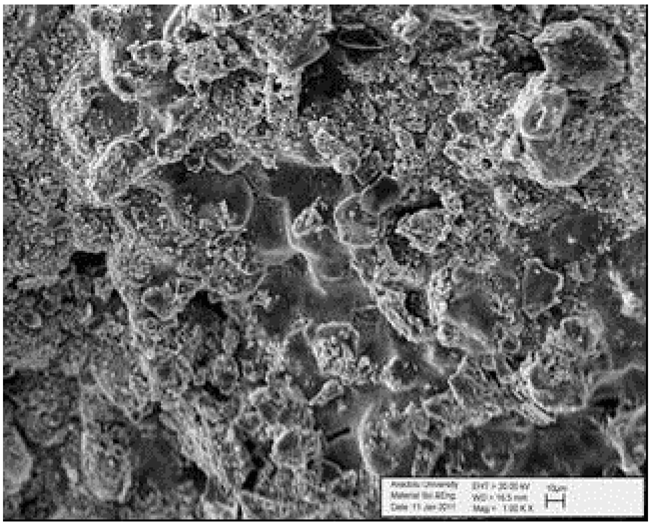

Fig. 13. *The fracture surface image of M-10H%-5S% refractory material.*

In general, those specified structural changes occured in the microstructure, occurrence of either transgranular cracks or intergranular cracks, significant reduction in MgO grain size were important parameters to improve the mechanical properties of MgO-hercynite-spinel composite materials (Figure 13).

IV. CONCLUSIONS

The strength, elastic modulus, fracture toughness, and surface energy values of MgO-hercynite-spinel composite refractory materials were generally close to each other and lower than MgO-Hercynite (M-H) refractory material.

MgO-hercynite-spinel (except M-5H%-5S%) had lower fracture toughness values than MgO-hercynite refractory materials. 1.5 times improvement of the fracture toughness and fracture surface energy values have been achieved compared to M-%5H material.

The of MgO-hercynite-spinel composite refractory materials had higher work of fracture values than pure MgO-hercynite material with low additive amounts (5 %, 10%), but generally became lower with increasing amount of hercynite. 2-fold improvement in work of fracture value of M-10H%-S%5 material was achieved compared to M-5H% material.

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