The Effect of Y_2O_3 Addition on Thermal Shock Behavior of Magnesium Aluminate Spinel

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Abstract:

The effect of yttria additive on the thermal shock behavior of magnesium aluminate spinel has been investigated. As a starting material we used spinel (MgAl₂O₄) obtained by the modified glycine nitrate procedure (MGNP). Sintered products were characterized in terms of phase analysis, densities, thermal shock, monitoring the damaged surface area in the refractory specimen during thermal shock and ultrasonic determination of the Dynamic Young modulus of elasticity. It was found that a new phase between yttria and alumina is formed, which improved thermal shock properties of the spinel refractories. Also densification of samples is enhanced by yttria addition.
Keywords: *Spinel, Yttria, Additive, Thermal shock*

1. Introduction

There is an increasing interest in ceramic materials with improved high temperature mechanical behavior for structural applications at high temperatures[1-4]. Spinel is a very promising structural material for mechanical and thermal applications because of its excellent high-temperature properties such as strength, hardness and chemical stability [5]. However, a low thermal shock resistance of spinel ceramics remains the limiting factor for its widespread applications. Mechanical and thermal shock properties of spinel refractories can be improved by addition of Y_2O_3 [6,7]. However, the literature does not provide a complete study of the influence of the addition of Y_2O_3 on thermal shock behavior of magnesium aluminate spinel. The present work describes the effects of addition of Y_2O_3 (0, 1, 3, 5 wt. %) on thermal shock behavior of magnesium aluminate spinel and possibility of using a nondestructive method for thermal shock analysis. The standard laboratory procedure, water quench test, was applied to determine the thermal stability behavior of the samples. The thermal shock resistance is measured in terms of the number of cycles that a refractory material can withstand when subjected to sudden temperature changes. Destruction of the samples surfaces was analyzed using the results of image analysis of samples before and during thermal stability testing.
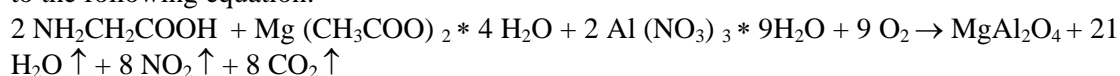
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2. Experiment
2.1. Materials

The spinel was obtained by a modified glycine nitrate procedure(MGNP).The glycine nitrate method (GNP) is based on the exothermal redox reaction between the fuel (glycine) and oxidizer (nitrate). The procedure needs to be performed in three stages, which are as follows: dissolution of metal nitrates and glycine in water, autoignition of the solution at about 180°C that afterwards undergoes the self-sustaining combustion giving ash as a product, and finally calcination of ash to burn out organic components.

In our work this method has been modified by partial substitution of nitrate with acetate in order to achieve better control of the combustion reaction. The reactants used for the synthesis were amino-acetic acid (glycine), aluminum-nitrate and magnesium-acetate mixed according to the following equation:

$$2 \, NH_2CH_2COOH + Mg \, (CH_3COO)_2 * 4 \, H_2O + 2 \, Al \, (NO_3)_3 * 9H_2O + 9 \, O_2 \rightarrow MgAl_2O_4 + 21 \, H_2O \uparrow + 8 \, NO_2 \uparrow + 8 \, CO_2 \uparrow$$

The MGNP obtained spinel powder was calcined at 800°C for 4 hours and then used for obtaining samples with 0, 1, 3 and 5 wt % of Y_2O_3, denoted as SY0, SY1, SY3 and SY5, respectively. Homogenization of the powder was achieved by attrition milling with Al_2O_3 balls in ethyl alcohol as media for 24 hours. The green bodies were pressed into cylindrical pellets of 10 mm in diameter and about 10 mm height using a uniaxial hydraulic press at a compaction pressure of 60 MPa and followed by isostatic compaction pressure of 110 MPa and sintered in air at 1500°C for 2 hours.

The bulk densities of the sintered samples were determined by the Archimedes method. Structural analysis was carried out by a Siemens D500 powder diffractometer. CuKα radiation was used in conjunction with a CuKβ nickel filter.

2.2. Thermal shock investigation

The thermal stability of the refractories was determined experimentally by the water quench test (JUS.B.D8.306). Samples were in the form of cylinders with 1 cm in diameter and 1 cm height. The samples were dried at 110°C until constant mass and then transferred into an electric furnace at 950°C where they were held for 40 minutes. The samples were then quenched in water at room temperature, left for 3 minutes and dried before returning to the furnace at 950°C. This procedure was repeated until failure and the number of quenches to failure was taken as a measure of thermal shock resistance. The failure is defined according to the standard test as destruction of 50 and more percent of samples surface area related on the sample surface before quenching. The used experimental method was similar to the procedure described in PRE Refractory Materials Recommendations 1978 (PRE/R5 Part 2).

2.3. Monitoring the damaged surface area in a refractory specimen during thermal shock

The samples were photographed by a digital camera before and after the water quench test. The samples surfaces were marked by different colors, in order to obtain a better resolution and difference in damaged and non-damaged surfaces in the material. A non-damaged surface, P0, was considered as an ideal surface of the sample using the common equation ($P_0 = d^2 \pi / 4$). The diameters of the samples, d, were measured using the Image Pro Plus program as well as the damage of sample surfaces [8]. The results of the material destruction test were given as function of the number of quench experiments.

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2.4. Ultrasonic determination of the dynamic Young modulus of elasticity

The ultrasonic pulse velocity test (UPVT) was used for determination of the dynamic Young modulus of elasticity before quenching [9-13]. Briefly, the pulses of longitudinal elastic stress waves were generated by an electro-acoustical transducer that was held in direct contact with the surface of the refractory under test. After traveling through the material, the pulses were received and converted into electrical energy by a second transducer. The pulse velocity, v, was calculated from the distance between the two transducers and the electronically measured transit time of the pulse as:

$$v(m/s) = \frac{L}{T} \tag{1}$$

where L = path length (m) and T = transit time (s).

By determination of the bulk density, the Poisson's ratio and ultrasonic velocity of a refractory material it is possible to calculate the dynamic modulus of elasticity using the equation given below :

$$E_{dyn} = v^2 \rho \left(\frac{(1 + \mu_{dyn})(1 - 2\mu_{dyn})}{1 - \mu_{dyn}} \right) \tag{2}$$

where v is the pulse velocity (m/s), ρ is the bulk density (kg/m^3) and μ_{dyn} is the dynamic Poisson ratio.

Measurement of ultrasonic velocity was performed using the equipment OYO model 5210 according to the standard testing procedure (JUS. D. B8. 121.). The transducers were rigidly placed on two parallel faces of the cylindrical sample 1 cm in diameter and 1 cm height using vaseline grease as the coupling medium. The ultrasonic velocity was then calculated from the spacing of the transducers and the waveform time delay on the oscilloscope.

Results and Discussion

The results of the material destruction test were given as a function of the number of quench experiments. Some photographs are given in Fig.1.
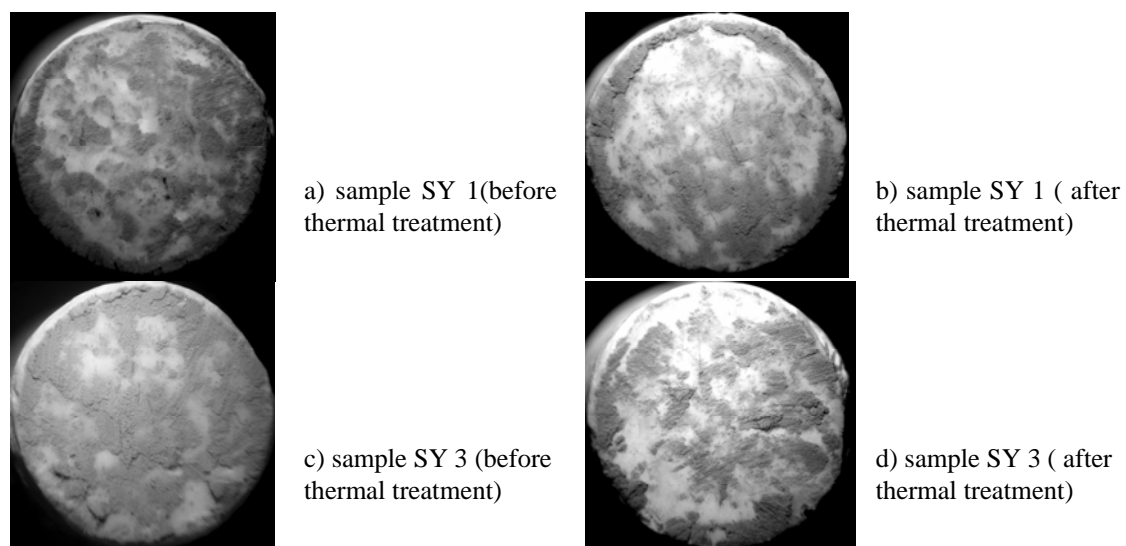

a) sample SY 1(before thermal treatment)

b) sample SY 1 (after thermal treatment)

c) sample SY 3 (before thermal treatment)

d) sample SY 3 (after thermal treatment)

Fig. 1 Photographs of samples under thermal shock experiment, white area is non damaged surface, dark area is damaged surface

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The white area represents the damaged surface and the dark area is the non-damaged surface. Sample SY3 (Fig.1d.) shows better thermal shock resistance than sample SY1 (Fig.1b.).

X – ray diffraction patterns of powders containing Y_2O_3 calcined at 800°C show the presence of two phases: spinel and Y_2O_3 (Fig. 2.). The samples sintered at 1500°C (Fig. 3.) show presence of the spinel ($MgAl_2O_4$, JCPDS number 21-1152), $YAlO_3$ (JCPDS number 33-0041) and traces of $Y_3Al_5O_{12}$ (JCPDS number 08-0178) and MgO (JCPDS number 04-0829).
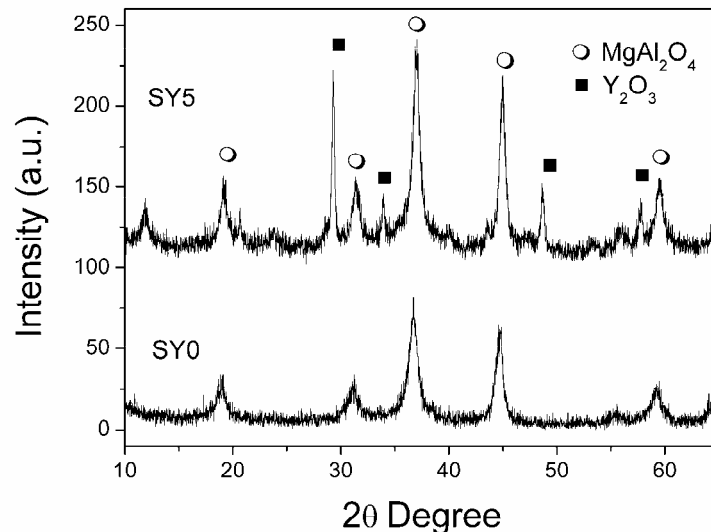

Fig. 2 XRD patterns of SY0 and SY5 powders before sintering

The phase compositions of the sintered samples determined from the XRD patterns presented in Fig. 3, are as follows:
SY1 sample shows the presence of spinel and traces of $Y_3Al_5O_{12}$.
SY3 sample shows the presence of spinel, $YAlO_3$ and traces of $Y_3Al_5O_{12}$.
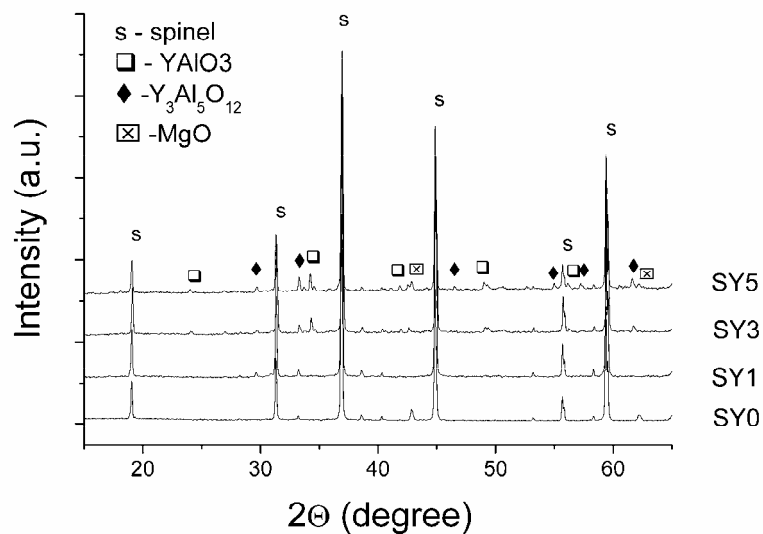SY5 sample shows the presence of spinel, $YAlO_3$, $Y_3Al_5O_{12}$ and MgO.

Fig. 3 XRD patterns of samples sintered at 1500 °C

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The added Y_2O_3 reacts with the spinel and produces $YAlO_3$ and $Y_3Al_5O_{12}$ by extracting Al ions from the spinel. Consequently, Mg/Al ratio in the spinel increases with an increase of amount of Y_2O_3, i.e. the spinel became enriched with Mg ions.

Tab. I Relative densities of samples doped with Y_2O_3

Sample	SY0	SY1	SY3	SY5
TD %	89.4	94.2	94.5	92.4

Tab. I shows the relative densities of samples doped with Y_2O_3 and sintered at 1500°C. The composition of samples without additive resulted in the relatively pore density < 90 TD %. The presence of Y_2O_3 enhances the densification. Since yttrium takes the Al^{3+} ion from the spinel structure, which generates lattice strain and improves mass transfer and densification. We found that the optimal concentration of additive was 3 % in current experimental condition.

YAlO$_3$ possesses better thermal shock resistance than the spinel. Due to the thermal expansion mismatch between the spinel (7.45×10^{-6}/°C) [14] and $YAlO_3$ (5.59×10^{-6}/°C) [14] significant level of micro-cracks were induced in spinel bodies. During the thermal cyclic treatment of the sample these micro- cracks reduced stress concentration at grain boundaries. With an increase in the micro-crack density after the thermal shock, the crack interaction effects became more important. The high thermal shock resistance was attributed to the interlinking of high level of pre-existing micro-cracking occurring in the spinel materials [15,16]. The best thermal shock resistance was obtained for SY3 samples, Fig. 4.
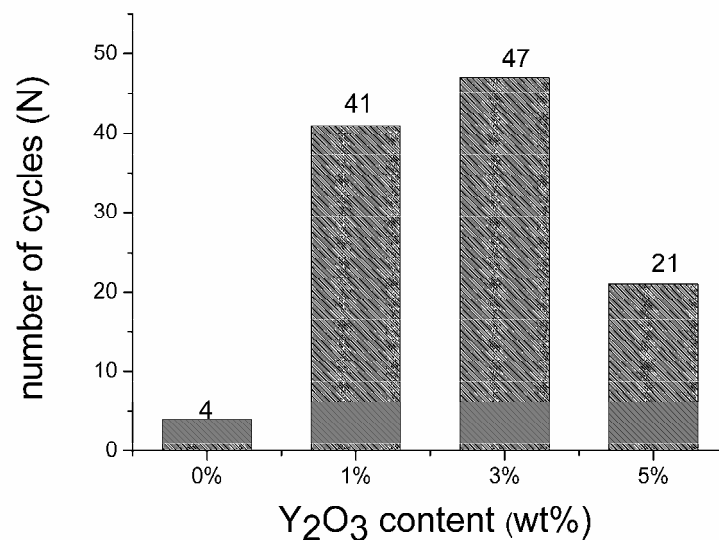

Fig. 4 Number of quenches to failure vs. Y_2O_3 content

The results given at the Fig. 5 showed that during quenching the damage to the original surface did not exceed 50 %. It is evident that the surface damage trend is the highest for sample SY3 and increases with the number of cycles of the thermal treatment.
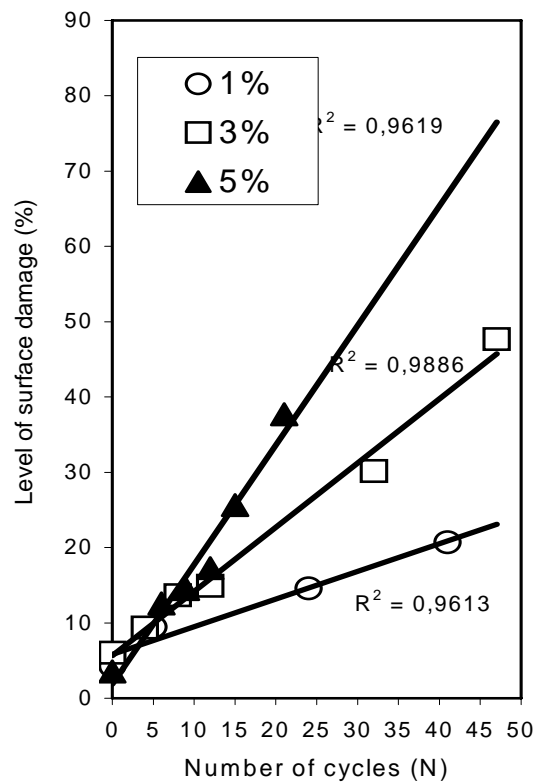
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Fig. 5 Level of surface damage vs. number of cycles

        The formation of cracks decreased the velocity of ultrasonic pulses traveling through the refractory because of their dependence on the density and elastic properties of materials. Decreasing of the Young's modulus occurred because of the high levels of pre-formed thermal expansion mismatch micro-cracks already present in the structure.
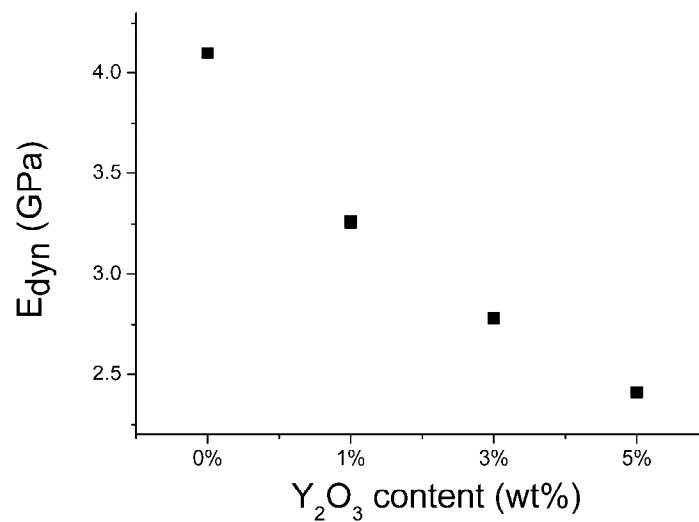

Fig. 6 Dynamic Young modulus of elasticity vs. Y_2O_3 content (before quenching)

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Conclusions

The results of the thermal shock investigation showed that increase of the amount of Y_2O_3 additive significantly influenced the densities as well as the thermal shock resistance of spinel. Yttria reacts with spinel forming the new phase ($YAlO_3$) with the lower thermal expansion coefficient compared with the spinel and thus causes the residual stresses, which is beneficial for the thermal cycling. The maximum number of quenches before failure in terms of high resistance to thermal shock was found to be 3% of yttria additive.

Acknowledgement

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Садржај: У овом раду је испитивана отпорност спинела, $MgAl_2O_4$, према термошоку у присуству Y_2O_3 као адитива. Као полазни материјал коришћен је спинел добијен модификованом глицин–нитратном методом. Анализа синтерованих узорака подразумевала је одређивање фазног састава, праћење оштећења површине узорака услед термошока, одређивање динамичког Јунговог (Young) модула еластичности ултразвучном методом. Нађено је да реакцијом спинела са Y_2O_3 долази до формирања нове фазе која побољшава отпорност спинелне керамике према термошоку. Такође је утврђен позитиван утицај додатка Y_2O_3 на денсификацију спинелне керамике.
Кључне речи: Спинел, итријум, адитив, термални шок.