Evaluation of Thermo Mechanical Properties of Zircon-Alumina-Magnesia Composite in the Field of Refractory Application

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ABSTRACT

This project is based on the evaluation of thermo mechanical properties of Zircon-Alumina-Magnesia composite in the field of refractory application. Hard, dense and volume stable Zircon-Alumina-Magnesia refractory bodies were prepared from appropriate mixture of graded Alumina, Zircon and Magnesia powder and fired at 1540^{0}C.Magnesia content pf fired bodies should be in such amount that is enough to combine with all the silica from dissociated zircon to form forsterite, and the zircon in the monoclinic form. Zirconia material is incorporated as the reinforcing phase to improve mechanical properties of alumina along with the superior thermo-mechanical properties (e.g. RUL, TSR and HMOR). The addition of MgO increases the amount dissociation of zircon and same time association of SiO_2 which reacts with either MgO or alumina forms forsterite and mullite. The formation of zirconia and Mg_2SiO_4 phase improved the thermal shock as well as HMOR.

INTRODUCTION:

Zircon ceramics is characterized by high refractoriness and thermal and chemical resistance in acid media and in metal and glass melts. It has many excellent properties such as good chemical stability, low thermal expansion coefficient (4.1×10^{-6}C), low heat conductivity coefficient (5.1 W/m ^{0}C at room temperature and 3.5 W/m ^{0}C at 1000^{0}C) and very good corrosion resistance against glass melts, slag and liquid metal alloy. Such a combination of properties leads that the consumption of this material constantly increasing throughout the world in spite of the high cost of raw materials[1]. The property slag resistance of zirconia refractory is high not only due to small pore size but also due to chemical inertness of zirconia to both acidic and basic slag, similarly Zircon has wide range of application as a construction material in glass tank, in iron and steel production. In energy technology, as molds and cores in precision investment casting or as protecting coating or steel molding tools[2,3].

The dissociation of zircon is a solid-state reaction and the dissociation temperature varying between 1285-1700^{0}C resulting in different phase diagram. In the case of investment casting of high temperature alloy such as nickel-based super alloy or titanium aluminides requires temperatures exceeding 1600^{0}C which is close to the decomposition temperature of zircon. The decomposition reaction started at 1556^{0}C (approx.) and accelerates with increasing temperature[4,5]. Decomposed zircon again associates between 1278-1556^{0}C with a maximum reaction rate at above 1444^{0}C. Impurities present in the material decreases the eutectic temperature below the dissociation temperature[5,6]. The lowest formation temperature (1333^{0}C approx.) is higher than the lowest association temperature (1278^{0}C approx.). Thus, solid state reaction in most case is super imposed by the formation of a lower melting silicate liquid [5]

MATERIALS AND METHODS:

Brick pressing

- Alumina-Zirconia-Magnesia composite were prepared by using Zircon, Reactive and Tabular alumina as raw materials for the experiments.
- The butches were prepared by taking different grade of raw materials in proper proportion, so that net zircon content in the range of 7-25 wt.
- The flow diagram for the preparation of the composite was given in the fig.1. The raw materials were mixed with molasses in pan mixture for 10-15 min till the grains were coated with molasses.
- The fine fraction were added and mixed for 15-20 min with 0.5% dextrin. Mixing was continued till the desired workability was achieved.
- Brick were pressed in standard shape (230×115×75) in FSP-120T press. The green density of the brick was in the range of 3.2-3.35gm/cc.

Drying & Firing of Bricks

The bricks were air dried 10-12hrs and then oven dried at 110^{0}C for 1 day. The dried bricks were fired at different temperature in different tunnel kiln at 1500^{0}C and 1550^{0}C with 90-120min soaking time.

Physical Properties

1 ***Apparent porosity, Bulk Density & ASG***

Apparent porosity is a measure of the volume of the open pores into a which a liquid can penetrate, as a percentage of the total volume. However, measure of the true porosity, which also take into account the volume of closed pores, gives a reasonable idea of the texture of the material as well as sintering characteristics. The bulk density and apparent porosity of the sintered specimen were measured by Archimedes principle using water as the immersion liquid. Then the apparent porosity is calculated using the following formula: -

$$AP=(W-D/W-S)\times 100 \qquad (1)$$

Where, D = weight of dry sample,
S= weight of specimen suspended in water,
W= weight of specimen in air.

Bulk density defines the material present in a given volume. It is defining as,

$$B.D. =D/(W-S) \qquad (2)$$

The apparent specific gravity is given by

$$ASG=D/(D-S) \qquad (3)$$

2. ***Cold Crushing Strength (CCS):***

CCS is done hydraulic pressing machine (Toni Versal, Germany), 1000KN at rate of increasing load 10KN. The cold crushing strength of a material is the maximum load at failure per unit of cross-sectional area when compressed at ambient temperature and result is expressed in Kg/cm^2 or MPa. The test specimen should be 75mm cube refractory brick cutting from refractory shape preserving the original surface as far as possible.

$$\text{Cold crushing strength (CCS)}=\text{Load/Area}, \qquad (4)$$

3 *Permanent Linear Change (PLC):*

PLC is the change on reheating and cooling of the bricks give an indication of the volume stability of the product as well as the adequacy of the processing parameters during manufacturing. It is given by

$$PLC=(L_i-L_{f)}/L_i\times 100 \qquad (5)$$

Where, L_i= Initial length of material,
L_f=Final length of the material

4 *Thermal shock resistance (TSR):*

In this method the sample of dimension 230×113×65mm inserted into a furnace with carbon heating element. The temperature maintained in it at 950^0C within the accuracy of +/-10^0C. After heating the material is water quenched. The no of cycle after which the material undergoes crack is the thermal spalling or thermal shock resistance.

5 *Phase Analysis*

The phase analysis of the fired sample was carried by XRD which is a versatile, non-destructive technique that reveals detailed information above the matrix composition i.e., number of phase present, crystallographic structure and mineralogical phases of a natural or manufactured product. A powder diffraction pattern is characteristic of the substance and indicates the state of chemical combination. The semi-quantitative analysis of polymorphs is analysis by using Rikago software.

6. *Hot Modulus of Rupture (HMOR):*

HMOR is done in a machine, named NETZSCH (Germany) at 1500C at the rate of increasing temperature 5C/min. Specimen size is 25×25×150mm (height×breadth×length). It indicates the amount of load can be bear by refractory at elevated temperature (around 1400^0C). It is given by the formula,

$$HMOR=3F_{max}L/2bh^2 \qquad (6)$$

Where F_{max} is the applied load,
L is the span length,
b & h is breadth and height of the sample.

7. *Refractory Under Load (RUL):*

RUL is done by a electrical furnace which consist of heat tubes of corundum, magnesite, mullite having diameter in the range of 100 to 120mm (inside diameter) and about 500mm length and thickness about 10 to 15mm. machine we used is TON Industries, Germany. Load is applied 38.5kg at rate of 2kg/cm^2. Cylinder of height 50+/-0.5mm, diameter 50+/-0.5mm obtained by cutting or boring through the brick. The temperature is raised at the rate of 15^0C/min up to 1000^0c at a constant rate of 8^0c/min. The deformation temperature (Ta) is at which 6% deformation of the maximum height occurs.

Result and Discussion

1 Apparent porosity:

The apparent porosity of the alumina-zircon-magnesia composites fired at 1540C was given in the Fig-2. It showed the increment of porosity is dependent on the zircon content. The porosity increases with alumina content whereas the amount of zircon content decreases. The wide variation of porosity (10-20%) is due to low sintering temperature for higher alumina content composite. There is definitely new phase formation which reduces the porosity for higher zircon content.

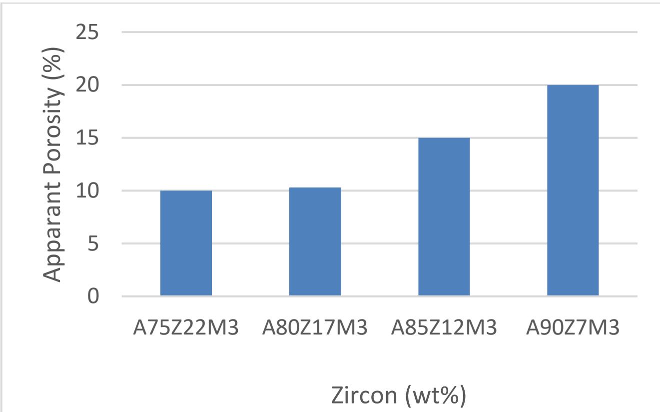

Fig3: Effect of Zircon addition on bulk density of alumina-zircon-magnesia composite

2 Bulk Density:

The Bulk Density of the alumina-zircon-magnesia composites fired at 1540C WAS GIVEN IN THE Fig-3. It showed the increment of Bulk Density is dependent on the zircon content range from 2.9 to 3.4 gm/cm^3 for the entire range of zircon. It is well understood the BD of the bricks decreases with zircon content as the true density of zircon is higher than the alumina. The density of the brick also dependent on the firing temperature, since the Al2O3 content for A90Z7M3 sample was 90% and therefore it needs higher temperature to increase the bulk density. However, foe all samples the coarse fraction was same and only the fine and ultrafine parts were changed.

3 Phase Analysis

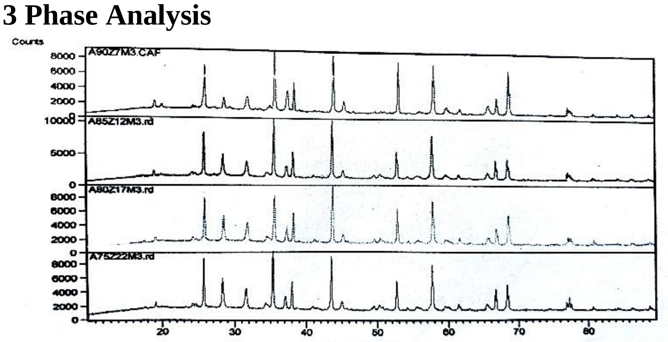

Fig-4: Phase Analysis of alumina-zircon-magnesia composites fired at 1540^0C

4 Cold Crushing Strength

The CCS of the alumina-zircon0magnesia composites was given in the Fig.6. The figure shows the increment in CCS is dependent on alumina content. The reason is, since CCS ha a linear relationship with density, higher the zircon content in the material (zircon has a higher density than alumina) higher is the CCS. But higher alumina in the composite shows higher lower strength due to the higher porosity as due to the firing temperature is low which was kept constant for all the composites.

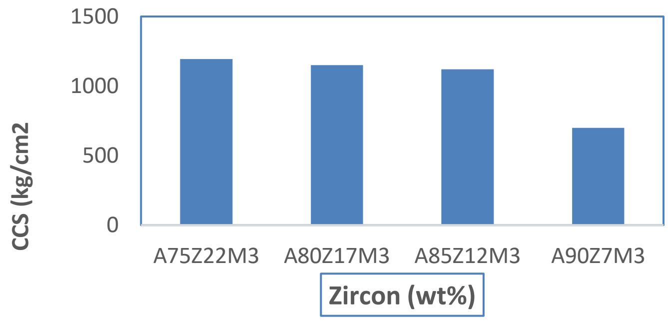

Fig-6: CCS as a function zircon content of alumina-zircon-magnesia composite

5 RUL

The RUL of the alumina-zircon-magnesia composite is given in the table 1. The deformation temperature increases with alumina content. The formation of $MgSiO_4$ phase in the composite lower than RUL however for higher alumina content composite have higher RUL through small amount of Mg_2SiO_4 present.

6 HMOR

The HMOR at 1400^0C of alumina-zircon-magnesia composites fired at 1540^0C was given in the table.2. The HMOR value increase with alumina content, however the higher porosity does not affect the strength value in higher temperature. The trend for the HMOR is similar that of the RUL value of the composite. Even through A90Z7M3 has lower density than the other three, HMOR is still higher and it can be MgO effects on the improvement of strength.

7 Thermal Spalling

The thermal spalling cycle of the alumina-zircon-magnesia composite from 1000C to water are given in the Table-3. The thermal cycles of the composite dependent on the phase formation, zirconia content and physical properties. The cracks formation in the brick with consequence cycles decrease with alumina content as porosity of the brick increases. A90Z7M3 sample did not show any distinct cracks even after 13nos of cycles. The higher spalling resistance can be the combined effect of micro-crack generation due to zirconia formation and new phase formation in the matrix act as resistance to crack propagation.

8. Conclusion

The alumina-zirconia-magnesia was prepared and the thermo-mechanical properties were evaluated which can be suitable for the refractory application due to the following findings:

1) The density of the composite increased with zircon content and the porosity is in the range of 10-20%.

2) The room temperature strength is porosity dependent and decrease with alumina content. High firing temperature required for the densification of high alumina content composite.
3) Thermal spalling resistance increase with lower zircon content as availability of SiO_2 is lower as compared to higher amount of zircon-alumina-magnesia composite.

4) HMOR is merely increase with zircon content in presence of MgO at 1400^0C. The dissociation of zircon forms zirconia and Mg_2SiO_4 phases.

Therefore, it may be concluded that alumina-zircon-magnesia composite are suitable than zircon-based composite for the application where high thermal spalling resistance is require

9. References:

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