Thermomechanical behaviour of alumina-mullite refractories developed by recycling industrial ceramic wastes

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ABSTRACT. Alumina-mullite (AM) refractories are widely used as liners for the thermal insulation of the combustion chambers in gas turbines for power production. A complete thermomechanical characterization of a commercial AM refractory was performed according to the international standards for dense ceramic or ceramic composites. Four-point flexural test were carried out on standard specimens to determine the values of Modulus of Rupture (MOR) and Young's modulus (E), at room temperature and up to 1500 °C: this temperature was chosen because the inlet temperature of the turbines for energy production was around 1400 °C. The most important property required to refractories for this application is the thermal shock resistance. In order to quantify it, four-point flexural tests at room temperature after quenching were carried out to calculate the residual MOR, according to the standard procedure for dense ceramics. The tests were performed with temperature differences up to 1000 °C, which is comparable to operating conditions during the turbine shutdown. New AM refractories were developed, by recycling a large amount (20 wt%) of industrial ceramic wastes coming from gas turbine investment casting process, and also adding zircon ($ZrSiO_4$). Also for these materials, a thermomechanical characterization was performed, in order to compare the behaviour of the new materials to the commercial refractory's one. Interesting results were found about the mechanical properties of the new materials. The refractories developed by recycling industrial ceramic wastes generally show better mechanical and thermal shock resistance than the commercial refractory taken into account.

SOMMARIO. I refrattari allumina-mullite (AM) vengono utilizzati come *liners* per l'isolamento termico della camera di combustione di turbine a gas utilizzate per la produzione di energia. Nel presente lavoro viene riportata la caratterizzazione termomeccanica completa di un AM refrattario commerciale, condotta secondo le norme internazionali per i materiali ceramici compositi o materiali ceramici densi. Sono state eseguite prove di flessione a quattro punti, per determinare i valori di modulo di rottura (MOR) e modulo di Young (E), a temperatura ambiente e fino la temperatura di 1500 ° C: questa temperatura è stata scelta perché la temperatura interna delle turbine per la produzione di energia è di circa 1400 °C. La principale proprietà meccanica richiesta ai materiali ceramici refrattari per questo tipo di applicazione è la resistenza agli shock termici. Per determinare tale resistenza, i campioni sono stati sottoposti a *quenching* in acqua e successivamente sono state condotte delle prove di flessione a quattro punti a temperatura ambiente, al fine di calcolare il MOR residuo. I test sono stati eseguiti con differenze di temperatura fino a 1000 ° C; tale condizione è paragonabile a quella che si realizza durante la fase di *shutdown* della turbina.
Sono inoltre stati sviluppati refrattari AM, riciclando una grande quantità (20% in peso) di rifiuti ceramici industriali, provenienti dal processo di *investment casting*, ed indagando altresì l'effetto dell'aggiunta di zircone

($ZrSiO_4$). Anche per questi materiali è stata eseguita la caratterizzazione termomeccanica, in modo da confrontare il comportamento dei materiali refrattari sviluppati con quello del materiale refrattario commerciale preso come riferimento. I refrattari contenti i rifiuti ceramici industriali mostrano, in generale, un miglior comportamento termomeccanico. E' stato inoltre verificato che l'addizione di zircone ad una miscela allumina-mullite ne incrementa sia la resistenza agli shock termici che la resistenza a flessione.

KEYWORDS. Combustion chamber liner; Alumina-mullite refractories; Flexural test; Thermal shock resistance.

INTRODUCTION

Only a few materials can be considered for the thermal insulation of combustion chamber in gas turbines; due to the operating conditions, they should have high thermal and thermo-mechanical properties. In particular, the critical service condition mainly occurs during the shutdown of the gas turbine, when the temperature of the combustion gas rapidly drops from about 1550 °C up to 450 °C [1].
Alumina-mullite refractories (AM) are widely used as liners in gas turbine. The typical microstructure of AM refractory is characterized by a coarse grains fraction (to induce porosity and increase thermal insulation) and a fine binder matrix [2]. This microstructure allows grain bridging mechanism which involves their excellent thermal shock resistance.
Thermal shock resistance of alumina-mullite refractories can be enhanced by zircon ($ZrSiO_4$) addition [3, 4, 5]. The starting decomposition temperature of pure zircon is about 1675 °C [6, 7] however the presence of impurities reduce the temperature at which the dissociation into ZrO2 and SiO2 occurs. As reported in literature [8], in alumina-mullite-zircon (AMZ) refractories, the SiO_2 formed by zircon decomposition can reacts with alumina to form mullite.
In this work, the mechanical and thermal shock resistance of AM and AMZ refractories produced by recycling ceramic wastes and of a commercial AM refractory (currently applied as liner of combustion chamber of power turbines) were studied.
The developed refractories show a better thermomechanical behaviour compared to the commercial refractory, taken as reference material (RM).

EXPERIMENTAL METHODS

A complete thermomechanical characterization of AM and AMZ refractories was performed according to the international standards for dense ceramic or ceramic composites.
Flexural test were carried out using a MTS electro-hydraulic testing machine in four-point configuration with a support roller span of 75 mm and a load span of 25 mm, according to international standards [9, 10]. Modulus of rupture (MOR) were determined at room temperature and up to 1500 °C, because the inlet temperature of the turbines for energy production was around 1400 °C and the liner surface temperature at flame side is between 1300 °C and 1550 °C [1]. MOR values were obtained by applying the follow equation reported below:

$$\sigma_f = \frac{3}{2} \cdot \frac{P(L_{out} - L_{in})}{WD^2}$$

Were P is the load at fracture, L_{out} is the length of support roller span, L_{in} is the length load span, W is the specimen width and D is the specimen thickness.
Thermal shock resistance was evaluated according to the standard EN 820-3 [11]. Four-point flexural tests at room temperature, according to the method previously described, were carried out after water quenching, in order to calculate the residual MOR. Shock tests were carried out at ΔT of 300 °C, 600 °C, 800 °C, 900 °C and 1000 °C. Quenching temperature of 1000 °C is comparable to the operating conditions during the turbine shutdown.
The standard dimensions of specimens for thermomechanical characterization are 5 x 12 x 85 mm^3. These specimens were derived from commercial tiles for the RM and from sintered tiles for the developed refractories. Developed refractories were obtained by mixing different grain size fractions of commercial alumina and of ceramic wastes. These wastes, coming from investment casting process, are composed of silica (55 wt%) and alumina (45 wt%) and are added to alumina in order to form mullite. In some case, zircon was added to alumina and ceramic wastes.

The studied refractory mixtures, called G4, GZ10 and GZ20 (Tab. 1) were cold isostatic pressed at 150 MPa and sintered at 1600 °C for 2 h in static air.
Apparent porosity and bulk density were measured using the water immersion method, according to the international standards [12, 13] and compared to the reference material.

	Mixtures		
Al_2O_3 grain size	**G4**	**GZ10**	**GZ20**
1mm ÷ 3.35 mm	27.1	27.1	7
45 μm ÷ 300 μm	19.2	19.2	13.2
45 μm ÷ 63 μm	19.2	19.2	10.6
$Ø_{50}$ = 0.8 μm	14.5	4.5	8.1
ZrSiO4 ($Ø_{50}$ = 1.1 μm)	-	10	20
Ceramic waste grain size			
Ø > 700 μm	10	10	-
250 μm< Ø < 700 μm	10	10	20

Table 1: Weight composition (wt %) of the studied refractory mixtures.

RESULTS AND DISCUSSION

Physical parameters as apparent porosity and bulk density of G4, G10 and G20 were determined and compared with the reference material (RM) (Tab. 2).

Samples	Water absorption (%)	Bulk Density (g/cm³)	Apparent porosity (%)
G4	7.7	2.7	21.0
GZ10	6.6	2.8	18.6
GZ20	6.1	2.9	17.6
RM	-	2.9 ± 0.1	18.5 ± 2.5

Table 2: Physical parameters of the refractory mixtures sintered at 1600 °C compared with the reference material (RM) .

Four-point flexural tests were executed at 20 °C, 1000 °C, 1200 °C, 1300 °C, 1400 °C and 1500 °C. For each temperature, at least two specimens were examined. As an example, stress-strain curves of G4 and GZ10 are shown in Fig. 1. Stress-strain curves show firstly a linear trend, while the pseudo-plastic behaviour starts close to the failure. Pseudo-plastic behaviour increases at higher temperature.

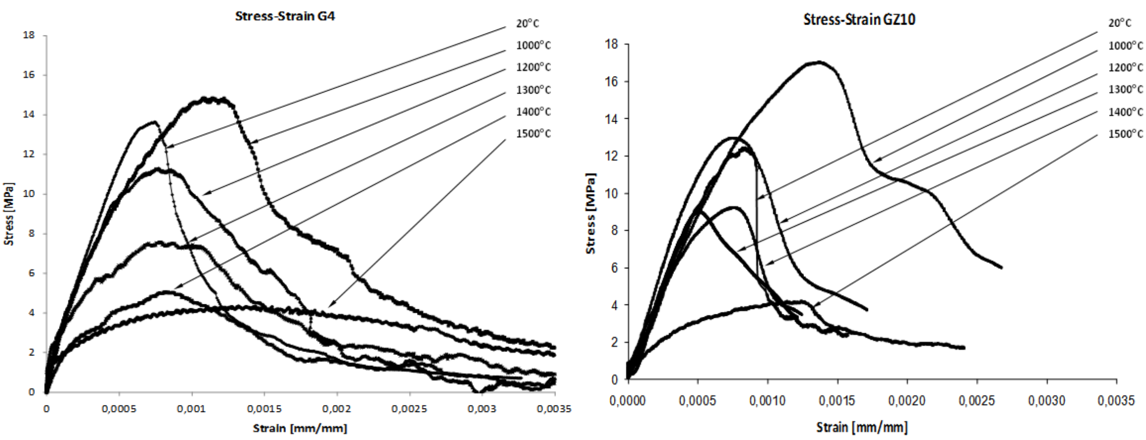

Figure 1: Stress-strain curves for the evaluation of thermomechanical properties of the refractory mixture G4 (left) and GZ10 (right).

Figure 2: G4 sample after four points bending test.

The MOR values of RM, G4, GZ10 and GZ20, calculated by flexural strength tests at different temperature, are reported on Fig. 3.
Developed refractories show better thermomechanical behaviour than reference one: MOR values of GZ20 is lower than RM only at 20 °C, while MOR values of G4 e GZ1 are higher than RM for each test temperature. For temperature above 20 °C, MOR values of GZ10 are higher than G4.
The slight increase of MOR of G4, GZ10 and GZ20 at 1000 °C is typical of materials containing mullite [14]. For all the materials, the mechanical properties decrease fast above 1000 °C: the high temperature promotes the plastic behaviour.
GZ20 showed the lowest flexural strength of refractories containing ceramic wastes, so only some temperatures were tested.

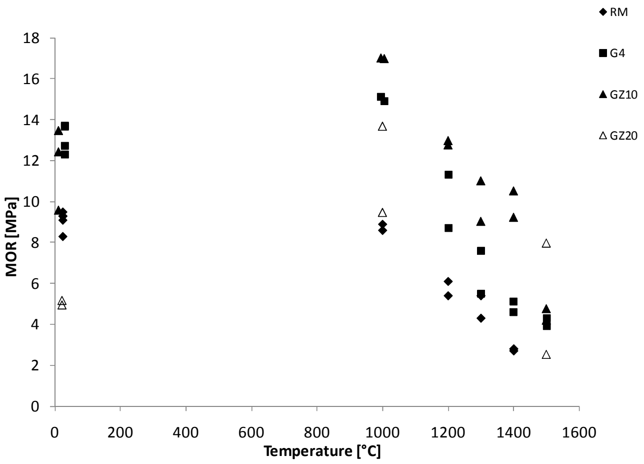

Figure 3: MOR values determined by the four-point flexural tests carried out on RM, G4, GZ10 and GZ20.

The residual MOR mean values determined on RM, G4, GZ10 and GZ20 after water quenching are shown in Fig. 4; critical quenching temperatures (ΔT_c) are also shown. According to standard EN 820-3 [9], critical quenching temperature is the temperature at which the mean strength is reduced by at least 30 % compared with the unshocked strength.

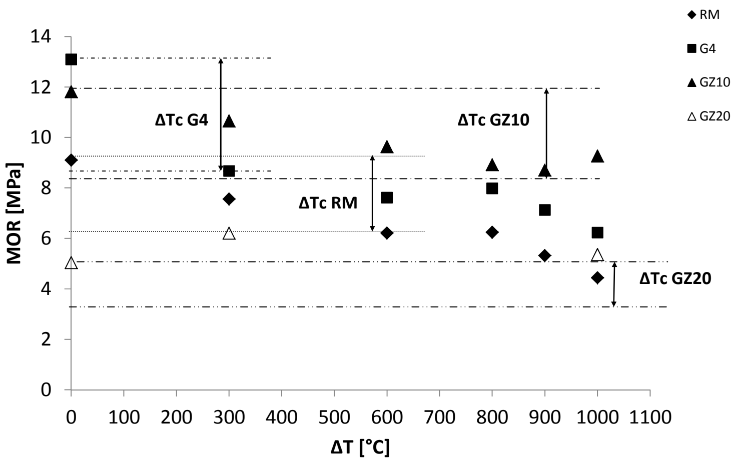

Figure 4: Residual MOR mean values determined on RM, G4, GZ10 and GZ20 after water quenching and their corresponding critical quenching temperature (ΔTc).

Generally, the stresses induced by quenching deteriorated the thermomechanical strength: the residual MOR values decrease with increasing shock temperature.
Residual MOR values for G4 and GZ10 are higher than RM ones for each quenching temperature. Moreover, after water quenching, GZ10 MOR is higher than G4 for each ΔT.
Although the residual MOR of GZ20 is the lowest among tested refractories (it is only comparable to residual MOR of RM), ΔT_c of GZ20 is the highest. Even after ΔT of 1000 °C, GZ20 retains the same flexural strength as before quenching. The ΔT_c of G4, RM and GZ10 corresponds to about 300 °C, 600 °C and 900 °C respectively. The best thermal shock resistance was obtained by GZ10, taking into account both the residual MOR values and the ΔTc.
Specimens of G4, GZ10 and GZ20 were not completely broken, also during flexural strength tests after quenching.

CONCLUSIONS

AM and AMZ refractories were produced by employing a large amount of ceramic wastes. Thermomechanical properties of the developed and commercial refractories were evaluated by flexural strength (at temperature up to 1500 °C) and by thermal shock resistance (ΔT up to 1000 °C). By the comparison of the thermomechanical behaviours, it was demonstrated that it's possible to improve the performance of a commercial AM refractory, even recycling 20 % of ceramic wastes.
Moreover, it was verified that the zircon addition can enhance the thermal shock resistance of the alumina-mullite refractories. The best results were obtained by GZ10 refractory (containing 20 % of ceramic wastes and 10 % of zircon): it showed the highest MOR values and residual MOR values of tested refractories.

ACKNOWLEDGEMENTS

This work has been done as a part of the Italian FIRB-MITGEA Project, supported by the Italian University and Research Ministry, Project No. RBIP064N2X.

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