

Variation of Poisson's ratio of refractory materials with thermal shocks

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Abstract

Investigations into the changes of Poisson's ratio as well as other mechanical properties of selected types of refractories subjected to thermal shocks have been carried out. The investigations included several types of porous refractory materials e.g. magnesia, magnesia–spinel, magnesia–chrome, chrome–magnesia, mullite, silica and low cement chamotte castable. The Poisson's ratio value of the examined materials decreased after each thermal shock. Decreasing of Poisson ratio caused by a stronger drop in Young's modulus than that for shear modulus was explained.

It was found that some tested materials were characterized by low values of Poisson's ratio, which after series of severe thermal shocks decreased even to negative values. In order to explain the observed phenomenon, an attempt to correlate the obtained results with the microstructure of materials before and after a series of thermal shocks was undertaken. A hypothetical model of the microstructure of a porous ceramic material with negative Poisson ratio was proposed.

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1. Introduction

Thermal shock resistance is an important feature of refractories, which frequently determines a possibility of their use in a thermal unit. The commonly applied method of thermal shock resistance examination, where a material is heated to a set temperature and next cooled with water or compressed air, does not allow predicting the material's behaviour in real thermal shock conditions. In real conditions, a working material has a different temperature gradient, due to one-sided heating and higher working temperature. Stresses in the material are also influenced by other factors, such as: mechanical properties resulting from the phase composition and the type of microstructure, i.e. spatial arrangement of phases, the shape and arrangement of pores, corrosive factors – crystallization of corrosion products in the working material's cooler zones as well as thermal shock intensity differing from that observed in tests, which is reflected in a different rate and degree of overcooling.

The complexity of this problem makes it necessary to adopt a different approach to investigations into refractories' thermal

shock resistance and develop a new method of testing this property of the material, which is so important in practical applications. Despite considerable technological advancement, this problem still remains unsolved, and searches for an appropriate method or groups of methods continue.

A number of interesting observations were made during the research works aimed at solving this problem, which were focused on improving the methods of determining or calculating the values related to thermal shock resistance of a material, such as: the criterion characterising microcracks propagation (R_{ST}), work of fracture (γ_{WOF}) [1], time of thermal stresses' relaxation τ [2], internal friction (Q^{-1}), Young's modulus (E) and shear modulus (G) as well as Poisson's ratio (ν). Among others it was found that in thermal shock conditions the drops in E and G values are accompanied by a decrease of Poisson's ratio, which in some cases may even reach negative values.

These observations gave the authors an idea of attempting to explain the drops in ν value and carry out further investigations into the changes of the above-mentioned properties of materials in the conditions of thermal shock with intensity similar to that in real working conditions.

First it was decided to examine the changes in properties of basic materials subjected to thermal shocks in the conditions of copper converter work. Due to the lack of precise data on the

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intensity of thermal shock that refractories are subjected to in these conditions, it was assessed on the basis of experiences of people dealing with refractories' application in the copper industry as well as on the ranges of temperature change in the converter process. It was assumed that the process temperature is 1350 °C and after the tapping it dropped to ca 700 °C, next a melted alloy at 1200 °C is poured in. This provided a basis for evaluating the intensity of thermal shock that refractory materials are subjected to as ca 11 °C/min. This assessment allowed the measuring station for examining the changes of mechanical properties to be modified.

The objectives of this work is an attempt to explain the observed phenomenon of Poisson's ratio drop to negative values in refractories subjected to a series of thermal shocks on the basis of the obtained results and literature reports.

2. Material and experimental procedure

The following industrially produced shaped and fired materials: magnesia–chromite, chromite–magnesia, magnesia–spinel, magnesia, mullite, silica and chamotte castable were used in the investigations. Samples for tests in a form of 230 mm × 64 mm × 12 mm plates were cut out from the shaped fired materials. Chamotte castable samples having the dimensions of 210 mm × 64 mm × 12 mm were cut after drying and next subjected to firing at 1000 °C, 1150 °C and 1300 °C. From each tested refractory materials a five to ten plates were cut from randomly chosen bricks and then samples were weighted, dimension of plates measured as well as internal friction (damping) and Young's modulus (Table 1). Standard deviation of Young's modulus of obtained plates varied from 1.4 GPa to 1.8 GPa depending on material. One plate from each tested material was chosen for thermal shocks experiments based on following criterion:

- best locking sample without visible damages;

- low value of internal friction (Q^{-1}), indicating lack of internal defects;
- close to average Young's modulus value.

Thermal shocks were conducted by heating the samples of magnesia–chromite, magnesia–spinel, magnesia, mullite, silica, and chamotte castable to 1000 °C at the rate of 8 °C/min and next annealed at this temperature for 4 h and cooled for 5 min with compressed air of 0.6 MPa pressure. The rate of cooling in these conditions was 230 °C/min.

The samples of magnesia–chromite and chromite–magnesia used in copper converters were subjected to thermal shocks by heating to 1000 °C at the rate of 8 °C/min, annealing at this temperature for 2 h and cooling in an insulation box for 270 min at the rate of 11 °C/min, until the temperature of 40 °C was reached. The experiment was repeated four or five times, depending on the type of material.

The value of E and G moduli, Poisson's ratio ν and internal friction Q^{-1} before and after each thermal shock was determined by a resonance frequency and damping analyser – RFDA (IMCE-Belgium), using the flexural and torsion vibrations. Determination was carried out according to ASTM E 1259 standard. The examined plates were placed on two rubber supports, having the shape of 5-mm diameter cylinders, located at the intersection of flexural and torsion vibrations' nodes. Such location ensures free vibrations of the plate and enables simultaneous determination of elastic properties. The points of inducing the vibrations and registering the frequency were selected so that the amplitudes of both types of induced vibrations were similar. The measurements of E , G , Q^{-1} and ν were taken 12 h after the thermal shock, i.e. in a relaxed condition. After a series of thermal shocks plates were weighted, dimension measured and its volume and apparent density calculated. Dimension and weight was measured with accuracy 0.02 mm and 0.01 g, respectively. It gave uncertainty of volume and apparent density calculation 0.3 cm³ and 0.005 g/cm³, respectively.

Table 1
Basic properties of the examined materials.

Property	Magnesia	Magnesia–spinel	Magnesia–chrome	Chrome–magnesia	Mullite	Silica	Chamotte castable (1400 °C)
Young's modulus (GPa)	93.3	31.0	58.9	48.8	71.6	8.5	33.2
Thermal shock resistance (number of cycles 950 °C/water)	4	14	8	8	84	0	20
R_{ST} (K m ^{1/2})	0.9	3.2	2.0	2.5	6.5	–	–
Work of fracture γ_{WOF} (J/m ²)	15.3	47.5	34.4	25.2	45.4	–	–
Thermal conductivity (W/mK)							
800 °C	–	3.8	3.6	3.2	1.69	1.37	–
1200 °C	3.2	2.9	3.5	3.1	1.85	1.77	–
Linear thermal expansion (%)							
300 °C	0.28	0.21	0.28	0.26	0.15		1.5 (900 °C)
1400 °C	1.92	1.52	1.53	1.48	0.75	1.2	
Open porosity (%)	17	18	17	19	16	21	18
Crushing strength (MPa)	45	60	68	45	68	45	40

Table 2

Changes of the value of E and G moduli, Poisson's ratio ν and internal friction Q^{-1} after subsequent thermal shocks of 230 °C/min intensity, measured after $t = 12$ h. $A_i - E$ or G value measured after thermal shock number “ i ”. $\Delta A = (1 - (A_i/A_{i-1}))100\%$.

Material	Cycle no.	E (GPa)	$(E \text{ } (\%))$	G (GPa)	$(G \text{ } (\%))$	ν	Q^{-1}
Magnesia	0	92.0 ± 0.5		42.9 ± 0.1		0.072 ± 0.011	0.0006
	1	68.2 ± 0.4	25.9	34.2 ± 0.1	20.3	−0.003 ± 0.010	0.0018
	2	56.2 ± 0.3	17.6	33.4 ± 0.1	2.3	−0.158 ± 0.008	0.0130
	3	42.0 ± 0.2	25.3	32.0 ± 0.1	4.2	−0.343 ± 0.007	0.0723
Magnesia–spinel	0	29.2 ± 0.2		15.9 ± 0.1		−0.085 ± 0.009	0.0115
	1	10.6 ± 0.1	63.7	6.2 ± 0.1	61.0	−0.150 ± 0.009	0.0128
	2	9.8 ± 0.1	7.5	5.8 ± 0.1	6.5	−0.165 ± 0.008	0.0163
	3	9.4 ± 0.1	4.1	5.6 ± 0.1	3.4	−0.168 ± 0.008	0.0221
Magnesia–chrome	0	59.0 ± 0.3		28.4 ± 0.1		0.039 ± 0.010	0.0022
	1	32.7 ± 0.2	44.6	17.1 ± 0.1	39.8	−0.042 ± 0.010	0.0025
	2	26.7 ± 0.2	18.3	14.5 ± 0.1	15.2	−0.083 ± 0.009	0.0046
	3	22.6 ± 0.2	15.3	12.8 ± 0.1	11.7	−0.114 ± 0.009	0.0082
Mullite	0	70.1 ± 0.4		30.4 ± 0.1		0.168 ± 0.012	0.0007
	1	61.7 ± 0.3	12.0	27.0 ± 0.1	11.2	0.143 ± 0.011	0.0012
	2	61.5 ± 0.3	0.3	26.9 ± 0.1	0.4	0.143 ± 0.011	0.0012
	3	61.4 ± 0.3	0.2	26.9 ± 0.1	0	0.142 ± 0.011	0.0012
Silica	0	8.5 ± 0.1		3.5 ± 0.1		0.219 ± 0.012	0.0160
	1	4.7 ± 0.1	44.7	2.1 ± 0.1	40	0.130 ± 0.011	0.0129

According to ASTM C 1259 standard the influence of particular variable on uncertainty of modulus calculation is as follows (uncertainty budget):

resonant frequency 0.2%,
sample length 0.3%,
mass 0.1%,
width 0.1% and
thickness 0.3%.

As a result the combined standard relative uncertainty 0.5% of Young (ΔE) and shear (ΔG) modulus were calculated. Using this value the uncertainty of calculation of Poisson ratio ($\Delta \nu$) based on partial derivative equation were determined (Tables 2–4).

Table 3

Changes of the value of E and G moduli, Poisson's ratio ν and internal friction Q^{-1} after subsequent thermal shocks of 230 °C/min intensity, measured after $t = 12$ h. $A_i - E$ or G value measured after thermal shock number “ i ”. $\Delta A = (1 - (A_i/A_{i-1}))100\%$.

Sample	Cycle no.	E (GPa)	ΔE (%)	G (GPa)	ΔG (%)	ν	Q^{-1}
Chamotte castable (1000 °C)	0	24.6 ± 0.2		11.3 ± 0.1		0.088 ± 0.011	0.0041
	1	22.5 ± 0.2	8.5	10.5 ± 0.1	7.1	0.073 ± 0.011	0.0028
	2	19.9 ± 0.1	11.6	9.5 ± 0.1	9.5	0.047 ± 0.010	0.0038
	3	19.0 ± 0.1	4.5	9.1 ± 0.1	4.2	0.043 ± 0.010	0.0045
	4	17.7 ± 0.1	6.8	8.7 ± 0.1	4.4	0.018 ± 0.010	0.0068
Chamotte castable (1150 °C)	0	29.4 ± 0.2		13.2 ± 0.1		0.114 ± 0.011	0.0033
	1	24.6 ± 0.2	16.3	11.4 ± 0.1	13.6	0.080 ± 0.011	0.0061
	2	19.9 ± 0.1	19.1	9.9 ± 0.1	13.2	0.006 ± 0.010	0.0155
	3	18.1 ± 0.1	9.0	9.3 ± 0.1	6.1	−0.029 ± 0.010	0.0205
	4	16.8 ± 0.1	7.2	8.9 ± 0.1	4.3	−0.054 ± 0.009	0.0257
Chamotte castable (1300 °C)	0	33.2 ± 0.2		14.9 ± 0.1		0.115 ± 0.011	0.0031
	1	27.8 ± 0.2	16.3	13.0 ± 0.1	12.8	0.069 ± 0.011	0.0071
	2	18.6 ± 0.1	33.1	11.0 ± 0.1	15.4	−0.154 ± 0.008	0.0241
	3	16.5 ± 0.1	11.3	10.5 ± 0.1	5.5	−0.209 ± 0.008	0.0279
	4	16.9 ± 0.1	−2.4	10.4 ± 0.1	1.0	−0.185 ± 0.008	0.0212
	5	14.6 ± 0.1	13.6	9.7 ± 0.1	6.7	−0.251 ± 0.008	0.0361

The microstructure of samples in their initial condition and after a series of thermal shocks was subjected to observation by examining resin-embedded microsections by means of the reflected light optical microscopy method. An optical microscope MeF2 with a Leica image analyser was used in the investigations.

Basic properties of the examined materials are given in Table 1.

3. Results

3.1. Determination of elastic properties

In each case the first thermal shock turned out to be the most destructive for the examined materials, irrespective of its intensity (Tables 2–4). This effect was reflected in a drop of the

Table 4

Changes of the value of E and G moduli, Poisson's ratio ν and internal friction Q^{-1} after subsequent thermal shocks of 11 °C/min intensity, measured after $t = 12$ h. $A_i = E$ or G value measured after thermal shock number " i ". $\Delta A = (1 - (A_i/A_{i-1}))100\%$.

Sample of material	Cycle no.	E (GPa)	ΔE (%)	G (GPa)	ΔG (%)	ν	Q^{-1}
Magnesia–chrome annealed for 2 h	0	32.2 ± 0.2		15.0 ± 0.1		0.071 ± 0.011	0.0094
	1	22.4 ± 0.2	30.4	10.7 ± 0.1	28.7	0.045 ± 0.010	0.0070
	2	19.8 ± 0.1	11.6	9.9 ± 0.1	7.5	0.042 ± 0.010	0.0088
	3	18.0 ± 0.1	9.1	8.7 ± 0.1	12.1	0.028 ± 0.010	0.0108
	4	16.2 ± 0.1	10.0	8.0 ± 0.1	8.0	0.016 ± 0.010	0.0123
Chrome–magnesia annealed for 2 h	0	48.4 ± 0.3		21.9 ± 0.1		0.106 ± 0.011	0.0050
	1	43.3 ± 0.3	10.5	19.9 ± 0.1	9.1	0.091 ± 0.011	0.0023
	2	42.6 ± 0.3	1.6	19.6 ± 0.1	1.5	0.085 ± 0.011	0.0021
	3	41.0 ± 0.3	3.8	19.1 ± 0.1	2.6	0.072 ± 0.011	0.0029
	4	39.6 ± 0.2	3.4	18.7 ± 0.1	2.1	0.060 ± 0.011	0.0037

values of E and G moduli, Poisson's ratio ν and increased value of internal friction Q^{-1} . It is worth emphasizing that the drops in G value compared to that of E modulus were in each case lower, which may indicate that tensile and compressive stresses connected with modulus E in thermal shock conditions have a more destructive effect in comparison with shear stresses related to modulus G .

Different values of ΔE and ΔG are reflected in the change of coefficient ν , which results from the dependence correlating these three values:

$$\nu = \frac{E}{2G} - 1 \quad (1)$$

This provides a basis for concluding that in thermal shock conditions the greater the effect of tensile and compressive stresses compared to shear stresses, the greater is the drop of Poisson's ratio values.

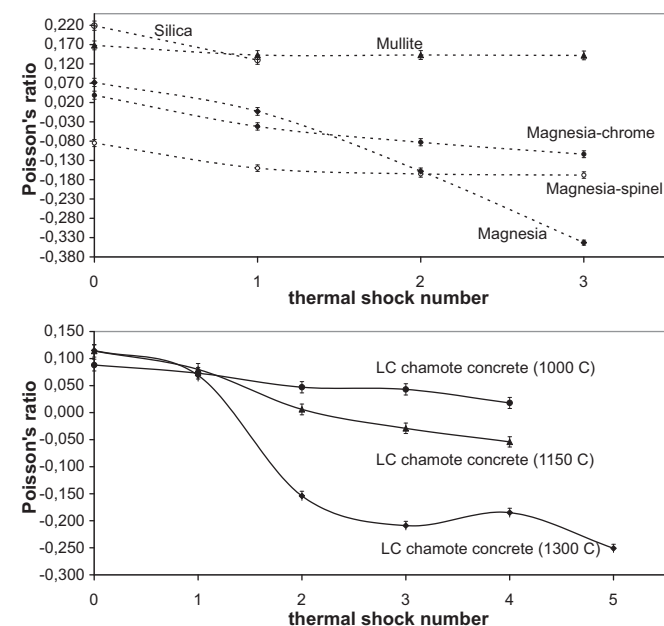


Fig. 1. Changes of Poisson's ratio after a series of thermal shocks of 230 °C/min intensity.

Changes of Poisson's ratio ν under the influence of thermal shocks for all the examined materials have been given in Figs. 1 and 2.

The magnesia–spinel material, having the highest thermal shock resistance among the examined basic materials, was characterised by the greatest changes of ΔE and ΔG after the first shock (Table 2). Following the subsequent thermal shocks the changes of ΔE and ΔG were the smallest. On the other hand, each thermal shock in the magnesia material, having the lowest resistance among the examined basic materials, caused similar changes of ΔE , whereas the changes of ΔG were the greatest after the first shock. This resulted in the greatest changes of ν . The magnesia–chrome material had intermediate properties. Internal friction Q^{-1} was observed to increase in this group after each thermal shock. Moreover, it was found that the initially low values of ν positive for the magnesia and magnesia–chrome product and negative for the magnesia–spinel one, dropped after the first thermal shock and decreased further with each subsequent shock. The same phenomenon was observed in experiments on magnesia–chrome and chrome–magnesia materials, carried out in the conditions of low intensity shock 11 °C/min (Table 4 and Fig. 2). In this case the drops of E , G and ν values, and an increase in Q^{-1} were visibly lower than for a shock of 230 °C/min intensity, which proves the influence of thermal shock intensity.

The mullite and silica materials were characterised by the expected values of Poisson's ratio before a thermal shock, which reached 0.168 for the mullite product and 0.22 for the silica one. These values decreased after the first thermal shock,

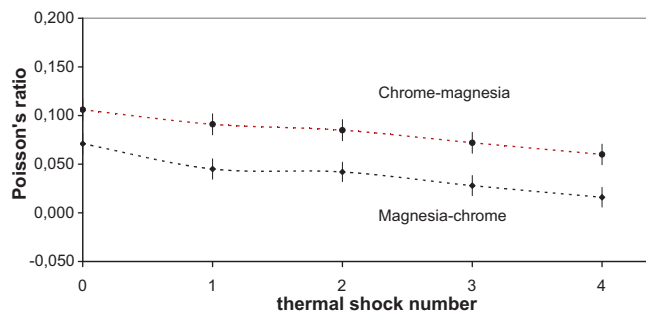


Fig. 2. Changes of Poisson's ratio after a series of thermal shocks of 11 °C/min intensity.

Table 5

Volume and apparent density of the examined materials before and after a series of thermal shocks.

Material	Volume V (cm ³) ± 0.3 cm ³		Mass m (g) ± 0.01 g		Apparent density ρ_p (g/cm ³) ± 0.005 g/cm ³	
	Before	After	Before	After	Before	After
Magnesia	173.6	175.0	490.36	490.14	2.825	2.801
Magnesia–spinel	178.5	179.6	507.31	506.87	2.842	2.822
Magnesia–chrome	177.9	179.8	554.58	554.80	3.117	3.086
Mullite	170.6	170.8	428.05	427.82	2.509	2.505
Silica	179.1	184.0	335.51	335.03	1.873	1.821
Chamotte castable (1000 °C)	160.7	161.9	348.70	348.58	2.170	2.153
Chamotte castable (1150 °C)	158.1	160.8	346.13	346.04	2.189	2.152
Chamotte castable (1300 °C)	160.6	161.7	354.87	354.68	2.210	2.193
Magnesia–chrome annealed for 2 h	176.6	177.1	552.66	552.27	3.129	3.118
Chrome–magnesia annealed for 2 h	171.8	172.1	539.21	538.88	3.139	3.131

maintaining however a relatively high positive value of 0.143 for mullite and 0.130 for silica material (Table 2, Fig. 1). After a series of subsequent thermal shocks, the mullite material practically did not change its E , G , Q^{-1} and ν properties (Fig. 1), whereas the examined silica material was destroyed after the first thermal shock. The obtained results for the mullite material, characterised by high thermal shock resistance, and for the silica material, which in fact was not resistant to thermal shocks due to phase transformations, are not surprising.

The initially low values of Poisson's ratio, dependent on the firing temperature, were observed in chamotte castable (Table 3). The value of Poisson's ratio changes after thermal shocks was also determined by castable firing temperature. The biggest drops in ν , reaching negative values (-0.251) were observed in case of castable fired at 1300 °C

3.2. Influence of thermal shocks on material microstructure

All tested refractory materials after a series of thermal shocks suffered loosening of microstructure observed by

increasing of samples volume, decreasing of mass and apparent density (Table 5). Observed decreasing of sample mass was a result of spalling of some materials grains caused by thermal stresses. Increasing of sample volume (measured by changes of linear dimensions) was a result of changes in material microstructure e.g. microcracks and channel like pores generation.

Magnesia and magnesia–chrome materials have been shown in Figs. 3 and 4 as the examples of microstructural changes in refractories subjected to thermal shocks. The observed difference in the microstructure of the magnesia product before and after thermal shocks was connected with channel like pores generated during thermal shocks around magnesia clinker grains, which resulted in the product microstructure loosening.

Similar differences in the general view of microstructure before and after thermal shocks were found in the magnesia–chrome (Fig. 4) and magnesia–spinel material. An increased amount of channel like pores around thick-grain fraction was observed, which led to the microstructure loosening, causing

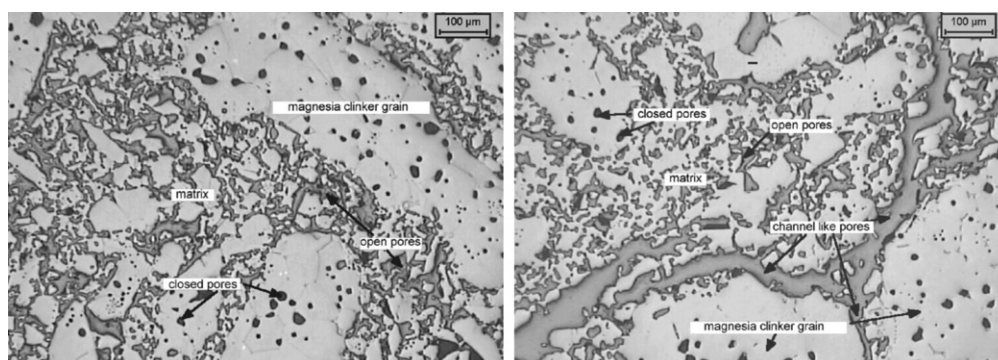


Fig. 3. Fine-crystalline microstructure of the magnesia material (left) before and (right) after thermal shocks of 230 °C/min intensity, with visible microstructure discontinuities in a form of channel like pores on the border of magnesia clinker grains.

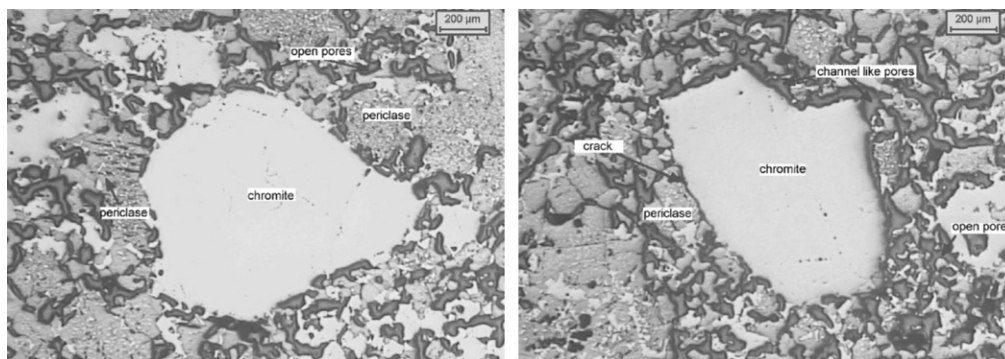


Fig. 4. Thick-crystalline microstructure of the magnesia–chrome material (left) before and (right) after thermal shocks of 230 °C/min intensity, with visible increased number of cracked direct bonds and channel like pores around coarse chromite grain after thermal shocks.

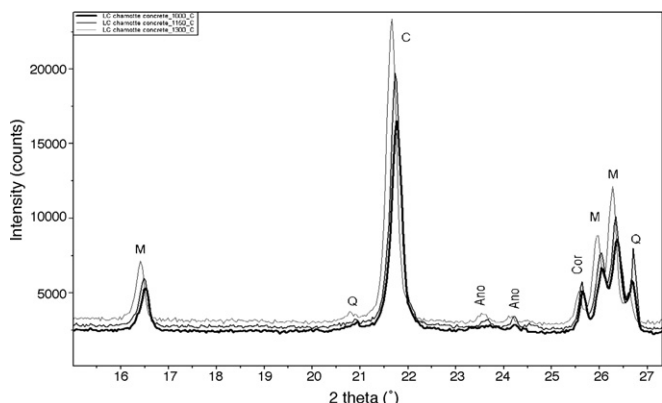


Fig. 5. Phase composition of low cement chamotte castable fired at 1000 °C, 1150 °C and 1300 °C after a series of thermal shocks, the main components of which are mullite (M), corundum (Cor), cristobalite (C) quartz (Q) and anorthite (Ano).

the so-called “rattle effect”. Generations of such defects could be direct cause of increasing of samples volume and decreasing of samples apparent density (Table 5).

Similar changes, involving the microstructure loosening were observed in all the examined materials.

The microstructure of the chamotte castable samples also became loosened as a result of thermal shocks, due to their

phase composition. Residual quartz and cristobalite were found in these samples. The amount of these phases was the greatest in the sample fired at 1300 °C, and the smallest in the one fired at 1000 °C (Fig. 5). Cristobalite at 250 °C is subjected to a reversible phase transformation $\alpha \rightleftharpoons \beta$, similarly to quartz at 573 °C. These transformations are accompanied by a considerable change of volume, which results in a higher number of cracks and greater loosening of the product microstructure. Mentioned observations stay in agreement with results presented in Table 5.

4. A model of material with a negative Poisson's ratio

The reasons for negative values of Poisson's ratio should be sought in the specific microstructure of refractories subjected to thermal shocks, which is characterized by solid particles (grains) of a particular shape, a system of pores, a net of cracks and the presence or lack of direct bonds.

The literature quotes examples of materials characterized by a negative Poisson's ratio [3]. Most frequently these are materials having a foam structure (high amount of pores). As an example, the behaviour of a foam material with a negative ν subjected to tensile stresses has been shown in Fig. 6.

Such behaviour of a material having a negative ν in case of refractories may be caused by the amount of voids

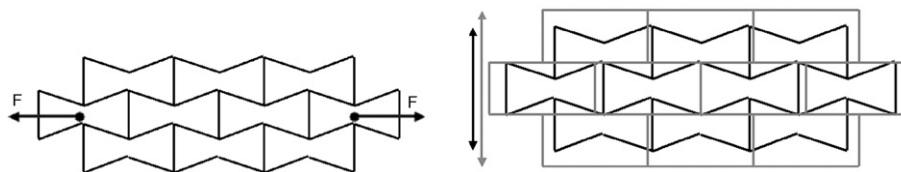


Fig. 6. A foam material with a re-entrant honeycomb cells (left), subjected to tensile stresses, which also caused the enlargement of perpendicular dimension in relation to tensile stress direction (right). Black colour – the initial condition, grey colour – the final condition.

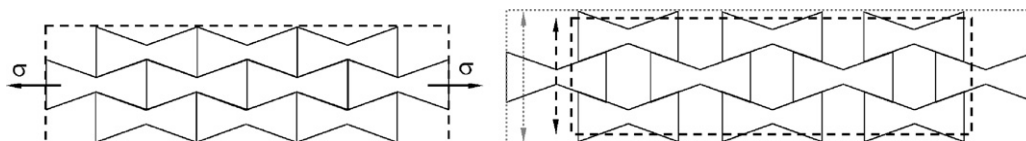


Fig. 7. A granular material having non bonded crystals in the shape of a re-entrant honeycomb cells (left), subjected to tensile stresses, which also caused the enlargement of perpendicular dimension in relation to tensile stress direction (right). Black colour – the initial condition, grey colour – the final condition.

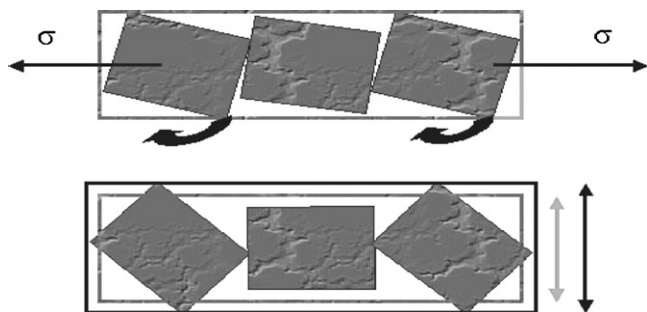


Fig. 8. A hypothetical ceramic material having a negative Poisson's ratio, built of rectangular (or cubic) grains of identical dimensions, which turn under the influence of tensile stresses.

(discontinuities) and defects, enabling a rotation or slight displacement of the material's grains due to tensile and compressive stresses. Such an idealised situation, which might take place in the defected and porous ceramic material has been shown in Figs. 7 and 8.

Drops in Poisson's ratio to negative values might then be related to additional defects in the material forming as a result of thermal shocks: an increased amount of voids, widening of pores and the formation of cracks. Such an assumption is justified by the obtained results, as the material's damage, reflected in the drops of E and G values and the growth of Q^{-1} , increases with the higher number of thermal shocks (Tables 2–4). The resonance method of measuring the values of E , G moduli, internal friction Q^{-1} , and particularly Poisson's ratio, due to its character and correlation with the material compactness, might be more commonly applied in refractory materials' research.

5. Conclusions

- The microscopic observations of refractory samples before and after thermal shocks indicate that thermal shock-related processes generate the microstructure discontinuity, chiefly in a form of channel like pores around the grains (the so-called “rattle effect”) and cracks related to brittle cracking. This explains the drops in the values of Young's modulus and

shear modulus, the increased internal friction and the lower values of Poisson's ratio.

- A microscopic analysis and sample mass and dimension measurements enables only a partial evaluation of microstructure changes, namely the phase composition and dimensions of particular aggregates of the product components.
- As a result of thermal shocks, modulus E decreases much faster than modulus G , what leads to a drop in Poisson's ratio. This proves the stronger effect of tensile and compressive stresses compared to shear stresses on the behaviour of materials in thermal shock conditions.
- Negative values of Poisson's ratio are most probably related to the specific loosened and defected microstructure of a porous material, which may cause a non-homogenous distribution of stresses. Owing to that a slight rotation or displacement of grains is possible in the conditions of the applied measuring method that introduces variable tensile, compressive and shear stresses.
- Poisson ratio for magnesia–chrome and chrome–magnesia materials in the conditions of thermal shocks characterised by 11 °C/min intensity, did not reach negative values, which indicates that the microstructure loosening is lower than in case of a thermal shock of 230 °C/min intensity.
- Poisson's ratio seems to be a good criterion of evaluating the material's compactness or the number of direct bonds. The use of Poisson's ratio determinations in refractory materials' investigations seems an interesting and prospective direction of research.

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