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Influence of the Phase Composition of Refractory Materials on Creep

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Abstract:

In this paper, the relationship between the creeping effect and mineralogical characteristics of the applied binding phase for various refractory materials (high-alumina materials, with high or low impurity content, tar bonded either magnesite or dolomite materials and silicate bonded chrom-magnesite materials) is presented. The mechanism of creeping is analyzed and the activation energy for creep for each investigated material is obtained and discussed. All investigated materials are creep sensitive under investigated conditions and have similar activation energies for creep except high-alumina refractories with a low impurity content.

Keywords: Thermal properties; Mechanical properties; Refractories; Activation energy for creep; Porosity

Introduction

Relative deformation of a material performed under the load, depends on various factors e.g. load intensity, time of exposure, temperature, structure of material etc. Regarding this problem a diversity of structural properties like grain size, porosity, phase distribution, crystal structure, crystal imperfections (point and line defects, cluster vacancies etc.) of the investigated material have a significant influence on creep [1-9].

The behaviour of refractory materials under high temperature load is highly affected by the presence of a glassy phase. The effect of a glassy phase is concentrated at grain boundaries and is expressed by changes of the boundary rheological properties of the system in the case when the glassy phase is wetting the grain boundary. If the level of wetting is low, then partial penetration of components of the glassy phase in the grain boundary causes weakening of the bonds between grains. If the concentration of the glassy phase and other phases with low melting points is high, then at elevated temperatures and under load the direct connections between grains are destructed and a continuous network made of phases with low melting points is formed. This causes weakening of bonds on grain boundaries and increases the sensitivity of refractory materials to creep.

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For quantification of the sensitivity of refractory materials to creep, it is essential to understand the behaviour of binder phases concentrated on grain boundaries and within inclusions.

For comparative analysis of the sensitivity of refractory materials to creep, under defined load and temperature conditions, besides strain, the energy activation for creep is a very important criterion and was therefore used to evaluate the investigated refractories.

2. Experimental

2.1. Materials

Five different commercial refractory materials were investigated in order to establish the most significant parameters that enhance material sensitivity to creep. The investigation was carried out using the following types of materials as ladle lining bricks:

- High-alumina refractories, produced by “Šamot”, Arandelovac, Serbia (HA_S) (with a high content of impurities);
- High-alumina refractories produced by “Didier”, Weisbaden, Germany (HA_D) (with a low content of impurities);
- Tar bonded magnesite refractories, produced by “Radex”, Rodenthein, Germany (TM_R);
- Tar bonded dolomite refractories, produced by “Silika”, Gostivar, Macedonia (TD_S);
- Silicate bonded chrome-magnesite refractories, produced by “Magnohrom”, Kraljevo, Serbia (CM_M).

2.2. Methods

The chemical composition of investigated refractories was established by standard chemical analysis. XRD analysis was carried out using a Philips 1710 diffractometer equipped with a copper anticathode ($\lambda=0.154178$ nm). XRD, light microscopy and EPM analysis were used in order to define the phases occurring in different lining bricks. All physical, mechanical and thermal properties were measured according to a standard procedure. For each sample the compressible strength, apparent density, open porosity, refractoriness, softening point, thermostability and remained shrinking were measured.

The creep test was performed using samples cut in a form of a cylinder having the same height and diameter of 50 mm. The samples were made in such a manner that the brick surface was one of cylinder basis while the other was cut out and polished to be parallel to the other.

All investigations were performed in a Netzch tube furnace designed for refractoriness and creep investigations. This type of furnace is equipped with a mechanism for load transfer, measurement and recording of temperature and strain. The samples were placed in the furnace under the load of 0.2 MPa. The furnace was heated up to 1000°C with a heating rate of 15°C/min, and with a heating rate of 8°C/min up to the maximum investigated temperature. The maximum temperature was 1400°C for the first investigation series and 1500°C for the second series. All specimens were held on the maximal temperature for 24h. Some samples were treated in a somewhat different manner. In the first series TD_S was heated up to the maximum temperature of 1350°C. In second series CM_M was creep tested at 1510°C instead of 1500°C and two samples of TD_S and HA_S were held only for 8 hours at the creep temperature.

Strain was measured for all investigated samples, and used for calculating the activation energy for creep.

Activation energy for creep is a significant parameter for evaluating the sensitivity of investigated systems to the creep process. The function that enables estimation of the activation energy in the conditions of constant load can be derived from the assumption that the following type of general function (ϕ) exists, describing the behaviour of the material within the entire creeping interval:

$$\phi = \left(T, \sigma, \varepsilon, \frac{\partial \varepsilon}{\partial \tau} \right) \quad (1)$$

where T is the temperature, σ is the stress, ε is the strain, $\frac{\partial \varepsilon}{\partial \tau}$ is the strain rate and τ is the time.

By analyzing the deformation tensor and stress tensor a simplified equation for creep in the previously defined shape (cylinder) and axial load was developed, using the assumption that viscose flow of a material is elasto-plastic giving the expression that defines the relation between function ϕ and deformation stress σ .

$$\phi = \sigma^2 \tau \quad (2)$$

On the other hand the relation between function ϕ and strain ε is given as:

$$\log \varepsilon = \log \lambda(T) + \alpha \log(\phi) \quad (3)$$

where $\lambda(T)$ is the boundary value of deformation for $\phi=1$. Coefficient α defines the deformation curve slope and might be in a certain way a kinetic parameter of deformation. Finally from the $\lambda(T)$ value it is possible to calculate the activation energy for creep using the equation:

$$\varepsilon(T) = \lambda_0 e^{\frac{-\alpha Q}{RT}} \quad (4)$$

where Q is the activation energy for creep, R is the universal gas constant, while λ_0 defines the value of function ϕ at $\varepsilon=1$.

Activation energy for creep according to equation (4) can be presented in the following analytical form:

$$\log \lambda_{T_1} - \log \lambda_{T_2} = - \left[\frac{\alpha Q}{R} \right] \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (5)$$

In this paper the function $\log \varepsilon = F(\log(\phi))$ was defined using equation (3) and α and $\lambda(T)$ were determined graphically. While values for α and $\lambda(T)$ obtained in this manner were used equation (5) was used for calculating the activation energy for creep.

3. Results and discussion

The results of chemical analysis are presented in Tab. I.

Tab. I Chemical composition of ladle lining bricks

Brick type	Chemical composition, [mass %]							
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Cr ₂ O ₃	TiO ₂	MeO ₂
HA _S	25.50	70.20	1.17	1.45	0.41	-	0.56	0.76
HA _D	26.50	72.40	0.54	-	0.21	-	0.11	0.26
TM _R	2.61	-	0.58	95.34	1.37	-	0.05	-
TD _S	1.01	1.40	0.31	43.82	52.74	-	-	-
CM _M	4.38	4.56	4.70	61.00	1.07	21.0	-	-

According to XRD, light microscopy and EPM analysis the following phases were identified in the investigated ladle lining bricks: HA_S- mullite, glassy phase, fajalite; HA_D- mullite, glassy phase, fajalite; TM_R- periclase, monticellite, forsterite; TD_S – periclase, CaO, tricalcium silicate, tricalcium aluminate, calciumalumosferrite, Brownmillerite; CM_M – periclase, chrompicotite, chrommagnesite, monticellite, merwinite.

Physical, mechanical and thermal properties for all investigated ladle lining bricks are given in Tab. II.

Tab. II Physical, mechanical and thermal properties of ladle lining bricks

Brick type	Compressible strength, [MPa]	Volume density, [g/cm ³]	Apparent porosity, [vol. %]	Refracto-riness, [°C]	Softening point, [°C]	Thermo-stability, [No of changes]	Remained shrinking (1773K for 2h), [%]
HA _S	54.50	2.50	20.50	1680	1650	20	0.27-0.30
HA _D	97.00	2.66	15.67	1750	1650	20	0-(0.9)
TM _R	58.24	3.13	4.20	1780	1650	-	-0.20
TD _S	27.50	2.75	8.90	-	1256	-	0.12
CM _M	23.71	2.94	22.40	1780	1650	18	1.00

Dependencies of strain on creeping time at different temperatures (1400 and 1500 °C), are given in Fig. 1, while Fig. 2 shows the dependence of the strain rate on creep time.

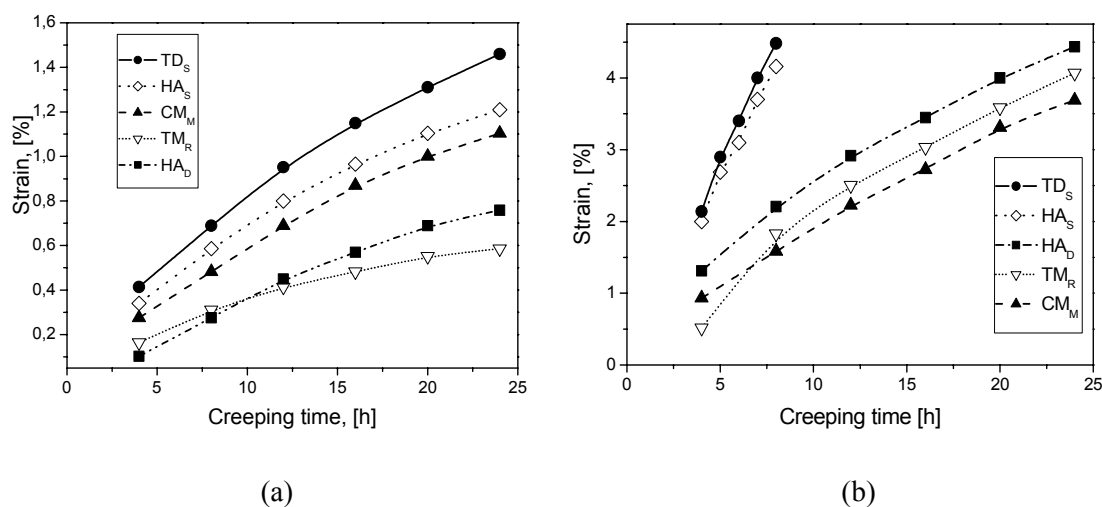


Fig. 1 Strain vs. creeping time, creeping temperature (a) 1400 °C, (b) 1500 °C

Curves presented on Fig. 1 (a) and Fig. 2 (a) are very similar indicating that the creep process occurs in a similar manner. After an initial period of 8-12h, all curves indicate that the creep process is in a stationary phase (phase of secondary creep), having an almost constant strain rate.

Fig. 1 (b) and Fig. 2 (b) indicate somewhat different behaviour. Some samples exhibit a significant change of the strain rate, while in the other samples the strain rate is more uniform ending with a state where change of the rate is minimal.

The highest change of strain rate was observed in high-alumina with a high content of impurities, (HA_S) and tar bonded dolomite (TD_S) samples.

The behaviour of refractory materials during creep depends upon process parameters and micro and macro structural properties. For the conditions applied in these materials

during the analysis of creep behaviour the macrostructural properties have the most significant influence, particularly porosity and composition of the bonding phase [10-13].

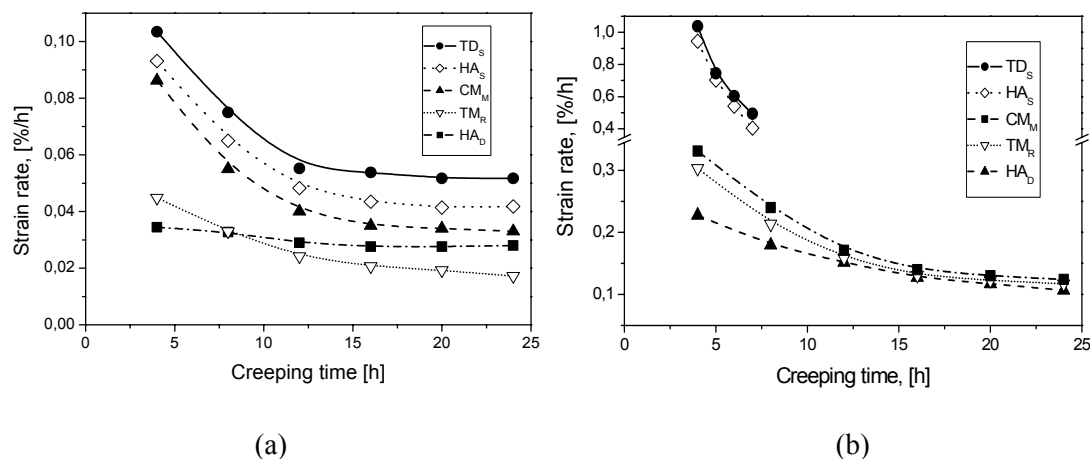


Fig. 2 Strain rate vs. creeping time, creeping temperature (a) 1400 °C, (b) 1500 °C

Analysis of the data presented on Fig. 1 (a) and Fig. 2 (a), while keeping in mind the phase composition of the sample HA_S obviously shows that at 1400°C material densification occurs. Densification occurred through slipping processes and grain rearrangement during viscoplastic flow of molten phases with low melting points i.e. glassy phase and fajalite, assisted by high porosity of the system.

Essentially the densification process (primary creep stage) is mainly completed during heating of the samples up to the experimental temperature. This is in accordance with the slight change of strain and strain rate within the first 8 hours of the creep test, followed by a period when the strain rate is constant (secondary creep stage).

There is significant similarity in the behaviour of high-alumina with a low content of impurities (HA_D) and high content of impurities (HA_S) at 1400°C. Differences in porosity and phase composition, especially the amount of phases with low melting points on grain boundaries, do not affect the behaviour of these materials during creep.

Quite contrary, at 1500°C the influence of the phase composition has greater importance on the behaviour of high-alumina refractories. High porosity of HA_S bricks together with a high content of the glassy phase and fajalite are responsible for intensive densification of samples, while the change of the strain rate is high.

High values of strain and strain rate are characteristic for glassy materials which at a given load and temperature continually change viscosity with time resulting in acceleration of creep of the material [1-5].

During deformation the phase composition can be changed by migration of FeO from the mullite lattice and decomposition of Fe₂O₃ to FeO + ½O₂, resulting in a decrease of viscosity of the binding phase and enhancement of the process of dissolving mullite on a given temperature [11, 15], and therefore intensifying the creep process of a material. In HA_D bricks due to the low impurity content the deformation processes are much slower, although in this material in the first stages the densification process is intensive. After 16 hours the steady-state stage is achieved, characterized by a slight change of strain with time and consequently a constant strain rate.

In HA_D samples the glassy phase and other melt forming phases with low melting points are present in a far smaller quantity as fine films wetting the mullite grains, which results in less dramatic changes in the material during the creep process compared with HA_S.

It is possible to establish from Figs. 1-2 that tar bonded dolomite (TD_S) bricks have similar curves of dependences of strain and the strain rate on time as HA_S samples. A previous investigation of dilatation under constant load of these materials [10] indicates that at a relatively low temperature (~1200°C) intensive shrinkage of samples occurs. This phenomenon is caused by a low content of SiO₂ that under load increases the concentration of Si-O-Ca bonds, by decreasing other types of bonds (with other cations present in the melt), resulting in formation of big cibotactic groups of molecules and increased concentration of C₃S. All these processes have a negative effect on the rheological properties of melts formed on grain boundaries of dominant phases of tar bonded dolomite materials [10, 12, 14, 15].

The process of regrouping of periclase grains and CaO and dominant silicate phases present within the binding phase of the material at 1350°C is somewhat slower and at the beginning of the process at the stage of primary creep the change of strain and strain rate depend on time, but after some time (12h), stationary flow of the material corresponding to a secondary creep stage occurs.

Also, at this temperature, it is expected that part of the occluded phases remain captured in closed pores of the system, especially in fine pores, slowing deformation of the material [10, 16]. Besides this, the gaseous phase by diffusion through melt along grain boundaries made of phases with low melting temperatures (i.e. various silicate phases) results in the increase of melt viscosity and in this way indirectly slows down the creep of the material up to the moment when the stationary condition and therefore secondary creeping stage is reached [1].

At 1500°C intensive flow of the material occurs, followed by high values of strain and the strain rate that is typical for glassy materials. Viscosity of the melt formed at grain boundaries is low resulting in intensive flow of the material [10]. Densification of the material is performed by viscoplastic flow of the glassy phase in surrounding pores, which at such high temperatures have mostly relaxed from occluded gaseous phases CO_x, released during combustion of tar [10, 16].

On the other hand, the creep curves of tar bonded magnesite materials at both 1400 and 1500 °C seem possible. Although within the material densification of the sample occurs already at 1200 °C, curves that define the dependence of relative deformation and rate of relative deformation on creep time, show that the creeping process passes through two stages: the stage of primary creep with intensive flow, where the rearrangement of materials and pore filling occur, in the process activated with the presence of a silicate phase with a low melting point such as monticellite and the phase of secondary creep with a roughly constant rate of relative deformation [14, 17].

In silicate bonded crommagnesite materials at 1510°C processes of rearrangement and intensive viscoplastic flow, have characteristics of primary creep, with continual change of rate with creep time. Also, it is obvious that after a defined time the strain slightly increases indicating the possibility of establishing a steady-state stage of the system for longer creep times ($\tau=24h$). The previous discussion of dilatation under load in the same system [10] indicates that densification of samples occurs already at 1350°C, due to the formation of silicate phases with low melting points (monticellite and merwinite) [10, 12, 14]. At a higher temperature (1510°C) significant migration of Fe²⁺/Fe³⁺ from the [(Mg, Fe)O·(Cr, Al)₂O₃] lattice occurs and concentration within the binding silicate phase occurs [2, 4, 5]. These processes result in less viscous melt consisting of phases with low melting points formed on spinel grains indirectly enhancing rearrangement and viscoplastic flow of the system. In this way the flow of material characteristic for primary creep is established with a tendency of transition to a steady-state after sufficient sample densification.

At lower temperatures (1400°C), this stage is reached after a certain time (12h). After the start of densification and filing of bigger pores, a further densification process is significantly slower and finally the steady-state flow of material has been reached. On the other hand, at higher temperatures due to the presence of increased quantity of melt of phases

with low melting points and enhanced rheological properties of the melt the flow of the material continues further with a prolonged non-steady-state character indicating that after a sufficiently long time (20-24h) the steady-state stage with characteristics of secondary creep was established.

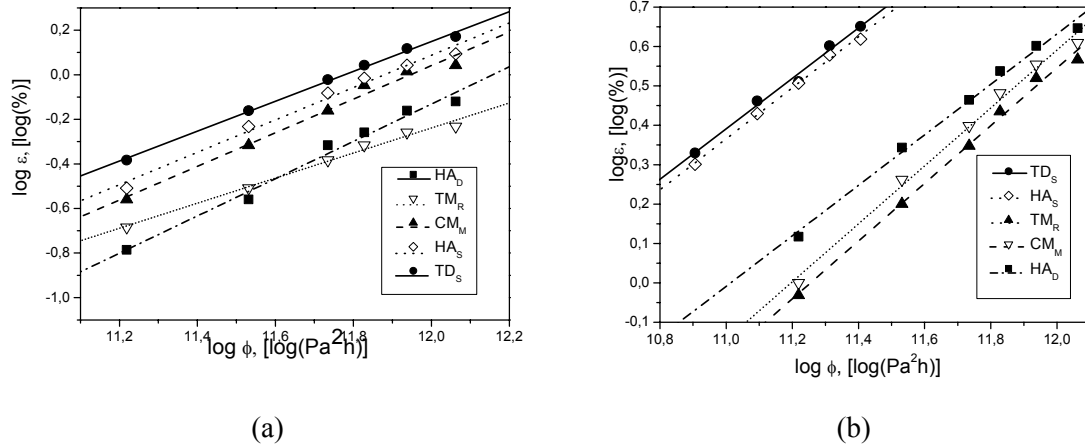


Fig. 3 Log ϵ vs. $\log\phi$, creeping temperature (a) 1400 °C, (b) 1500 °C

The dependence of $\log \epsilon$ (logarithm of strain) as a function of the logarithm of function ϕ was calculated according to equation (3) and is presented on Fig. 3. Experimental data was fitted with linear regression and the appropriate equations are given in Tab. III.

Tab. III Appropriate linear regressions

Brick type	Creep temperature [°C]	Equation	Correlation coefficient
HA _S	1400	$\log \epsilon = -8.454 + 0.726 \cdot \log(\phi)$	0.985
HA _D	1400	$\log \epsilon = -10.671 + 0.890 \cdot \log(\phi)$	0.993
TM _R	1400	$\log \epsilon = -8.945 + 0.732 \cdot \log(\phi)$	0.996
TD _S	1350	$\log \epsilon = -8.713 + 0.671 \cdot \log(\phi)$	0.991
CM _M	1400	$\log \epsilon = -8.734 + 0.754 \cdot \log(\phi)$	0.984
HA _S	1500	$\log \epsilon = -7.392 + 0.658 \cdot \log(\phi)$	0.996
HA _D	1500	$\log \epsilon = -7.691 + 0.679 \cdot \log(\phi)$	0.993
TM _R	1500	$\log \epsilon = -7.797 + 0.717 \cdot \log(\phi)$	0.997
TD _S	1500	$\log \epsilon = -7.264 + 0.668 \cdot \log(\phi)$	0.989
CM _M	1510	$\log \epsilon = -8.019 + 0.735 \cdot \log(\phi)$	0.993

The data given in Tab. III was used to determine values for α and $\lambda(T)$. Using these values and equation (5) the activation energy for creep was calculated and presented in Tab. IV.

Tab. IV Activation energy for creep

Brick type	Sample	Q, [kJ/mol]
High-alumina with high content of impurities	HA _S	378
High-alumina with low content of impurities	HA _D	936
Tar bonded magnesite	TM _R	344
Tar bonded dolomite	TD _S	392
Silicate bonded chrome-magnesite	CM _M	221

The values of activation energies for creep are for all investigated materials within a relatively narrow interval, indicating that all investigated systems are sensitive to creep and are not suitable for operating conditions where long-term load of materials on high temperatures such as the investigated ones occurs. The only exception from such a tendency was shown by high-alumina bricks with a low impurity content (HA_D), that had a significantly higher activation energy for creep compared to other investigated materials.

4. Conclusion

According to the results obtained for relative deformation and the rate of relative deformation of the investigated refractory materials (high-alumina with high and low impurity content, tar bonded dolomites, tar bonded magnesite and silica bonded chrome-magnesite materials), on temperatures from 1350°C to 1510°C, under constant load the following conclusions can be made:

- Especially high sensitivity to creep deformation was found at 1500°C for high-alumina refractories with a high impurity content and tar bonded dolomite materials.
- All the other investigated materials showed similar behaviour, characteristic primary creep, when rearranging of the material in large pores of the system occurs. This phase is followed by a secondary creep stage and material densification by viscoplastic flow.
- Plastic flow is the dominant mechanism in all stages of the process, due to the formation of a melt of phases with low melting points on grain boundaries of basic phases of the system.
- Activation energies for creep show high sensitivity to creep for all analyzed materials under investigated conditions except for high-alumina refractories with a low impurity content.

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Садржај: У раду је дата веза пузања ватросталних материјала и минералошких карактеристика везивних фаза за различите ватросталне материјале (високоалуминатне, катраном везане магнезитне, катраном везане доломитне материјале и силикатно везане хроммагнезитне материјале). Поред тога анализиран је механизам пузања и прорачуната је енергија активације процеса пузања за сваки од испитиваних материјала.

Кључне речи: Ватростални материјали, механизам пузања, енергија активације пузања, релативна деформација, брзина релативне деформације.
