JOURNAL OF MATERIALS SCIENCE 20 (1985) 4163–4168

Creep of CaO/MgO refractories

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The creep properties of a standard doloma brick (containing ~40% MgO) and a magnesia-enriched doloma product (containing ~60% MgO) have been compared with the behaviour of CaO–MgO samples having compositions and microstructures similar to those of the pellet raw materials used for manufacture of the fired doloma refractories. The creep strength is shown to be improved not only by magnesia enrichment but also by reducing the impurity levels, particularly the Fe_2O_3 content.

1. Introduction

Doloma, produced by calcining natural dolomite ($CaCO_3 \cdot MgCO_3$), is the most abundantly occurring and readily available basic refractory raw material. Yet, despite the widespread use of this type of refractory for service, little information is available on the strength characteristics of commercial doloma products. Since refractory materials are usually required to operate under stress for considerable periods at high temperatures, creep measurements provide a useful assessment of high-temperature strength. For this reason, the present investigation was designed to examine the factors affecting the creep properties of fired doloma refractories.

2. Experimental results

A standard doloma refractory was manufactured from natural dolomite which was calcined to produce pellets having a uniform dispersion of MgO crystals in a CaO crystal matrix (Fig. 1). The resulting pellet was graded, pressed to shape and fired at 1843 K to form a brick of ~16 to 20% apparent porosity. The analysis of the material is included in Table I and the brick microstructure is illustrated in Fig. 2.

Cylindrical testpieces, 51 mm long and 35 mm diameter, were core-drilled from the brick and the specimen ends ground flat and parallel before testing. All tests were carried out in air using compression creep machines which have been described elsewhere [1].

2.1. Creep behaviour of a fired doloma refractory

Under all conditions studied, after the initial strain on loading, the creep rate was found to decrease slowly but continuously with time, as illustrated by the creep curves shown in Fig. 3. Since a steady creep rate was not attained, even after creep strains of 0.20, the creep properties were considered by reference to the creep rate recorded at a true creep strain of 0.03. The results presented in Figs. 4 and 5 demonstrate that, as found for a wide range of crystalline solids [2], the variation of the creep rate, $\dot{\varepsilon}_{0.03}$, with stress, σ, and temperature, T, could be described using a power law expression of the form

$$\dot{\varepsilon}_{0.03} = A\sigma^n \exp(-Q_c/RT) \qquad (1)$$

with a stress exponent, n, of about 1.7 and an activation energy for creep, Q_c, of $430 \pm 25\,kJ\,mol^{-1}$.

2.2 Creep of doloma raw materials

The creep strengths of fired bricks are ultimately limited to those of the pellet raw materials from which the bricks are made. In order to provide an indication of the relative strengths of the fired doloma refractory and the appropriate pellet raw material, the creep properties of the fired brick (Fig. 4) can be compared with those observed for pellet-type materials produced from natural dolomite having a composition

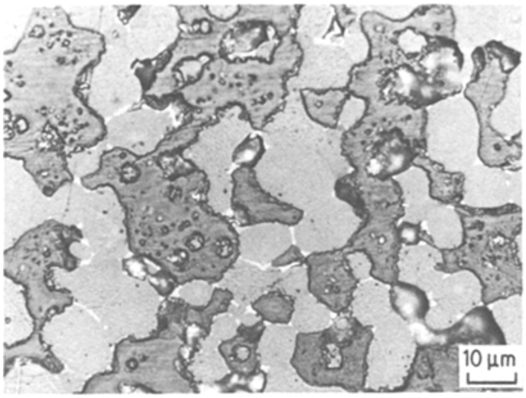

Figure 1 Microstructure of a typical doloma pellet particle in the fired doloma refractory ($\sim$40% MgO). The magnesia crystals appear lighter than the lime phase. A small volume fraction of silicate impurity phase can be seen, particularly at the MgO–MgO crystal boundaries.

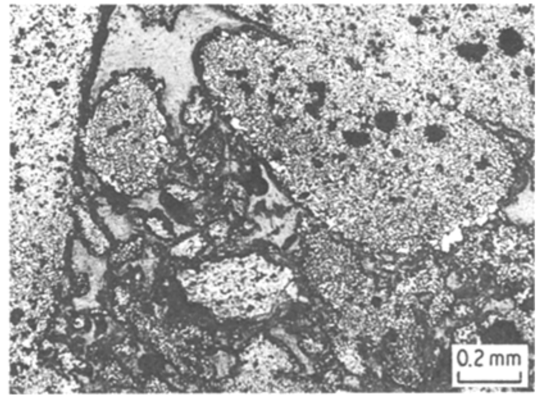

Figure 2 Microstructure of the fired doloma refractory ($\sim$40% MgO) showing larger polycrystalline MgO–CaO pellet regions existing in a matrix composed of fine doloma particles, silicates and pores.

close to that used during manufacture of the present doloma bricks (Table I).

It has been shown that, as with the fired doloma product (Fig. 3), the creep curves recorded for doloma pellet-type material were characterized by a continuous decay in creep rate with time [3, 4]. This similarity in creep curve shape therefore allows the relative strengths of the "pellet" raw material and the fired brick to be assessed by reference to the creep rates obtained at a strain of 0.03. The results obtained are shown in Fig. 6.

Although the maximum stresses which could be employed during testing of the brick samples were considerably below those studied for the pellet-type material [3, 4], several facts indicate that a direct comparison of properties is valid. Firstly, the activation energy for creep of the pellet material was similar to that found for the doloma brick ($\sim 430\,\mathrm{kJ\,mol^{-1}}$). Secondly, although an n value of over 3 was observed for the pellet at high stresses, the stress exponent recorded at low stress levels was similar to that for the doloma brick (i.e. $n \simeq 1.7$). Thus, in the low-stress range relevant to service conditions, the creep properties of the pellet raw material and the fired brick can be described using Equation 1, with identical values of n and Q_c. The data included in Fig. 6 therefore suggests that, at low stresses, the creep resistance of the fired brick is close to that of the equivalent pellet raw material. Since the pellet samples have a porosity of $\sim$5% compared with the $\sim$18% apparent porosity of the brick, it would appear that the creep strengths of doloma refractories decrease only slightly with increasing porosity over the range considered.

TABLE I Composition of doloma refractory bricks

Oxide	Composition (wt %)		
	Standard doloma	MgO-enriched doloma	Pellet material
SiO_2	0.9 to 1.3	0.8 to 1.2	0.49
Al_2O_3	0.3 to 0.6	0.3 to 0.5	0.031
Fe_2O_3	0.9 to 1.3	0.8 to 1.1	0.77
CaO	54.0 to 58.0	46.0 to 50.0	58.02
MgO	38.0 to 41.0	47.0 to 51.0	40.53

2.3. The effect of magnesia enrichment

Additional evidence supporting the direct comparability of the creep properties of the pellet-type material and the fired refractory brick (Fig. 6) was obtained by examining the effects of magnesia enrichment on the high-temperature strength of doloma. In this study, the results obtained for the standard doloma refractory (containing $\sim$40% MgO) were compared with those observed for a magnesia-enriched doloma brick (containing $\sim$50% MgO). Both bricks were produced in a similar manner but, in the case of the magnesia-enriched product, the pellet doloma was blended with the appropriate quantity of graded sea-water magnesia before pressing and firing. The full analysis is included in Table I.

As found for the pellet raw material and the standard doloma refractory, tests carried out

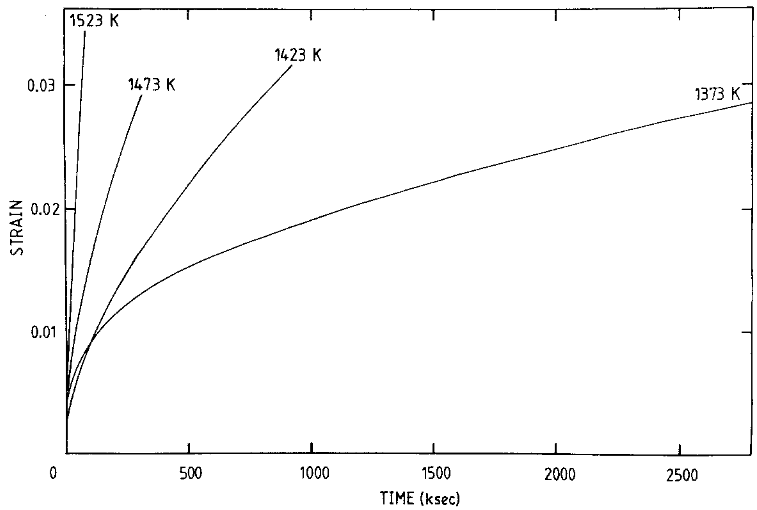

Figure 3 Creep curves recorded at $1.5\ MN\ m^{-2}$ for samples of a fired doloma brick tested in compression at temperatures of 1523, 1473, 1423 and 1373 K.

with the magnesia-enriched doloma established that the creep rate decayed continuously with time under all conditions examined so that, once again, the creep strength was assessed by reference to measurements of the creep rate at a strain of 0.03. The results obtained are shown in Fig. 7. Clearly, the stress dependence of the creep rate is the same for both materials even though the creep resistance at 1423 K is improved by a factor of about two by increasing the magnesia content from 40 to 50%. This level of improvement is fully consistent with previous evidence that the creep rate decreased almost linearly by about an order of magnitude as the magnesia content of CaO/MgO pellet-type samples was increased from 25 to 100% [3].

3. Discussion

The results presented in Figs. 3 and 7 provide an indication not only of the stresses which doloma bricks can sustain during high temperature service but also of the possible avenues for development of improved doloma products. Thus, for example, magnesia enrichment leads to an increase in strength (Fig. 7) as well as to improved resistance to slag and oxide attack [5]. In contrast, the data included in Fig. 6 suggest that comparatively little improvement in creep strength would be expected by modifying the production routes in an attempt to reduce the overall porosity. However, in addition to these direct conclusions, the present evidence also provides guidance as to the role of various impurities in determining the creep strength of doloma refractories. In particular, since similar behaviour patterns were observed for both the pellet-type raw material and the fired bricks (Fig. 6), the composition-dependence of the

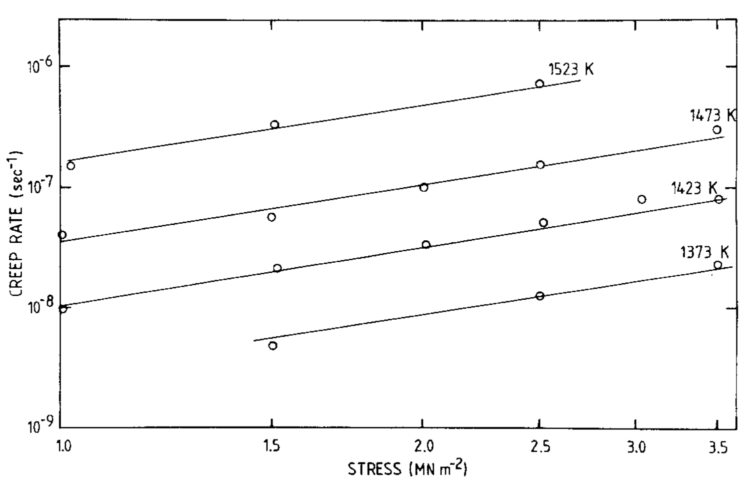

Figure 4 Stress dependence of the creep rate recorded at a true creep strain of 0.03 for samples of a fired doloma brick tested at 1523 to 1373 K.

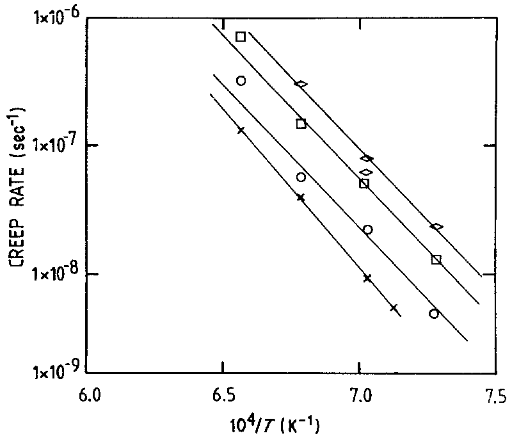

Figure 5 Temperature dependence of the creep rate recorded at a true creep strain of 0.03 for samples of a fired doloma brick at stresses of (×) 1.0, (○) 1.5, (□) 2.5 and (◊) 3.5 MN m^{-2}.

TABLE II Composition and creep rate of natural and synthetic pellet-type doloma

Specimen	Composition (wt %)				Creep rate ($sec^{-1} \times 10^6$)
	SiO_2	Al_2O_3	Fe_2O_3	CaO	
S1	0.19	0.02	0.11	54.0	1.0
S2	0.13	0.02	0.84	53.1	29.1
S3	0.18	0.22	0.08	53.3	1.6
S4	0.21	0.26	0.78	51.7	14.0
S5	0.57	0.01	0.07	52.2	1.2
S6	0.58	0.01	0.79	51.2	33.1
S7	0.60	0.13	0.08	52.8	1.8
S8	0.51	0.16	0.78	51.4	21.2
S9	1.71	1.02	2.90	50.2	28.3
N1	0.61	0.27	1.09	56.2	27.0

creep strength of fired refractory products can be inferred from the known effects of various impurities on the creep properties of pellet-type CaO–MgO materials [3, 4].

The effects of impurities have been examined using pellet-type materials produced from both natural and synthetic doloma [3]. The synthetic doloma samples were made from analytical grade $CaCO_3$ and high-purity $Mg(OH)_2$. These starting materials were calcined at 1573 K, pressed into bars (6.4 mm × 6.4 mm × 42 mm) and fired at 2073 K to give test pieces having porosities of 2 to 4% and average crystal sizes in the range 3 to 5 μm. The composition of the resulting synthetic doloma is given as Sample S1 in Table II. In order to consider the effects of variations in impurity level, test bars of different composition were then obtained by doping the pure starting materials with SiO_2, Al_2O_3 and/or Fe_2O_3. The different compositions studied are listed as Samples S2 to S9 in Table II, together with the creep rate recorded at a true creep strain of 0.03 during compression tests carried out for each sample at 62 MN m^{-2} and 1473 K [3].

The results presented in Table II suggest that silica additions had a relatively small effect, alumina had a greater influence and Fe_2O_3 proved to be particularly damaging, i.e. a marked deterioration in creep resistance was noted only with samples having high Fe_2O_3

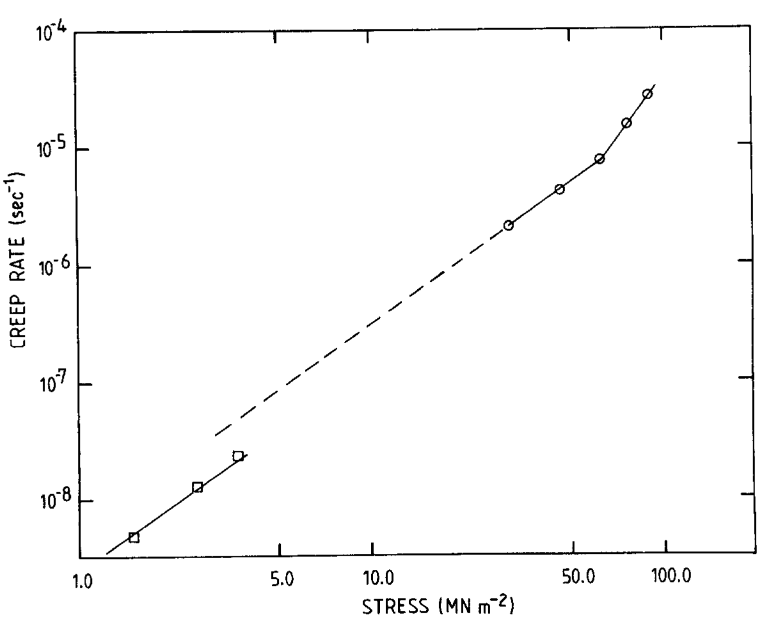

Figure 6 Stress dependence of the creep rate recorded at a true creep strain of 0.03, (□) for samples of a fired doloma refractory and (○) for specimens having a composition and microstructure comparable with those of the pellet raw material used for manufacture of the doloma brick. The results are compared at a test temperature of 1373 K.

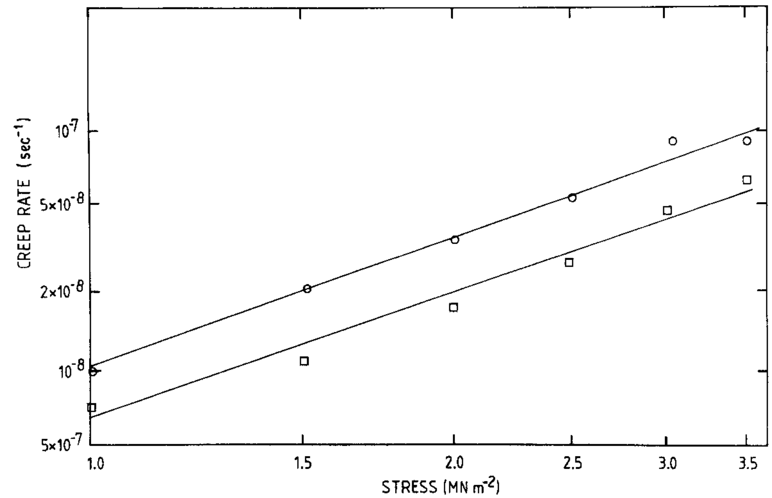

Figure 7 The stress dependence of the creep rates recorded at a true creep strain of 0.03, (○) for samples of a standard doloma refractory containing ~40% MgO and (□) a magnesia-enriched doloma brick containing ~50% MgO. All tests were carried out at 1423 K.

levels. Furthermore, the results obtained for these synthetic materials seem to be fully representative of the behaviour patterns which could be expected for natural doloma pellet. Thus, Sample S8 was made to have impurity levels approaching those of natural doloma pellet, Sample N1. Clearly, similar creep behaviour was then observed for these compositionally-equivalent natural and synthetic materials (Table II).

One further conclusion can be drawn from the data listed in Table II, namely that a distinct exhaustion effect was noticed such that successive increases in impurity content had progressively less effect on creep resistance [3]. This view can be illustrated by reference to the creep rates recorded for Samples S8 and S9. The latter sample was doped to almost twice the impurity contents of the natural doloma, (Sample N1) and the equivalent synthetic material (Sample S8), yet this large increase in impurity content caused little further decrease in creep resistance.

The similarity in creep properties of compositionally-equivalent natural and synthetic doloma (Table II) indicates that effects recorded for the synthetic samples would also be found for natural doloma pellet. Moreover, the creep characteristics of the pellet-type material appear to be the same as those observed for fired doloma brick of comparable composition (Fig. 6). It therefore follows that, of the commonly occurring impurities present in natural dolomite, the creep strength of fired doloma refractories would be improved substantially by minimizing the Fe_2O_3 content. With the conventional procedures used to produce doloma refractories from natural dolomite, the methods of improving purity are generally limited to the selection of raw material, coupled with relatively simple dressing operations, and to the use of low-ash fuels for dead burning [7]. A distinct limit is therefore imposed on the purity of natural doloma pellet. However, if the need for doloma products having superior creep strength is sufficient to justify the higher raw material costs involved, synthetic doloma refractories of high purity can be made from pellet produced using magnesia and lime as raw materials.

4. Conclusions

1. At temperatures in the range 1373 to 1523 K, the stress and temperature dependence of the creep rate of a fired doloma brick can be described using a power-law relationship of the form

$$\dot{\varepsilon}_{0.03} = A\sigma^n \exp(-Q_c/RT)$$

with $n \simeq 1.7$ and $Q_c \simeq 430\,\mathrm{kJ\,mol^{-1}}$. These values of n and Q_c are virtually identical to those observed for samples having microstructures and compositions similar to those of the pellet raw material used to produce the fired doloma refractory.

2. Enriching the magnesia content of the doloma brick from 40 to 50% MgO decreases the creep rate by about a factor of two under the same test conditions. This improvement in creep resistance is close to that found on increasing the magnesia content of pellet-type specimens.

3. Since the behaviour patterns observed for

the fired doloma refractories and for the pellet-type materials are virtually identical, information available on the creep characteristics of pellet-type specimens suggests that a substantial improvement in high-temperature strength would be achieved by decreasing the impurity levels, particularly the Fe_2O_3 content, of the raw materials used to produce the fired doloma products.

Acknowledgements

The authors wish to thank the Science and Engineering Research Council for financial support which included a Senior Research Assistantship for one of the authors (P.J.S.). The generosity of Steetley Refractories Ltd in producing the materials for this programme is also gratefully acknowledged.

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Received 19 December 1984
and accepted 15 January 1985