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Phase development and high temperature deformation in high alumina refractory castables with dolomite additions

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Abstract

The mechanical properties of refractory castables both at room and high temperatures are essential parameters for the selection of the operating conditions and the structural design of their components. Four spinel-containing matrix compositions in the high-alumina region of the Al_2O_3–MgO–CaO ternary diagram were selected and prepared by using dolomite additions. The creep behaviour of these matrices was studied in the temperature interval ranging from 1000 to 1400 °C. A correlation between the microstructural phase evolution and the creep behaviour with temperature was established.

Keywords: Castables; Spinel; Creep; Refractories

1. Introduction

The development of castables for ladle linings has contributed to a rapid increase in the demand for monolithic refractories in the field of iron and steel making. The addition of spinel to the castable compositions has improved resistance to slag corrosion and erosion.[1–4] Alumina-spinel castables have been developed for ladle refractories, resulting in major improvements in durability compared to traditional products. At the same time, the addition of magnesia (dead burned magnesite) to alumina castables to form spinel is also being observed with keen interest. Until now the addition of dolomite to high alumina refractory concretes has not received much attention in the literature. There is also a lack of information on the creep properties of refractory castables due to their chemical and mineralogical complexities.[5–12] Yet the creep test is a very important tool for refractory matrix engineering. It reflects the dynamic properties of refractory materials developed for structural applications.

The aim of the present work has been to investigate the high temperature deformation (creep) corresponding to the matrix of high-Al_2O_3 refractory castables with dolomite additions in the temperature range 1100–1400 °C. A study of the microstructural and phase evolution with temperature for all designed materials has been carried out.

2. Experimental procedure

Four refractory castables compositions were designed by using tabular alumina (T-60),[a] white corundum,[b] calcined alumina (CT 9SG and CL 370C),[a] dolomite[c] and calcium aluminate cement (CA 270).[a] The compositions were selected to obtain after a high temperature treatment (1650 °C) spinel contents of 5, 10, 15 and 20 wt.%.[13,14] Taking into account that the matrix of the castables constituted by the finer grain sizes is the main responsible of the high temperature deformation of the castables, the fraction with a grain size lower than 125 μm was considered as the matrix. To analyze the role of the matrix on the creep behaviour of these materials, the grain fraction of less than 125 μm was obtained by sieving the total refractory mixtures. A software was developed for calculating the theoretical chemical

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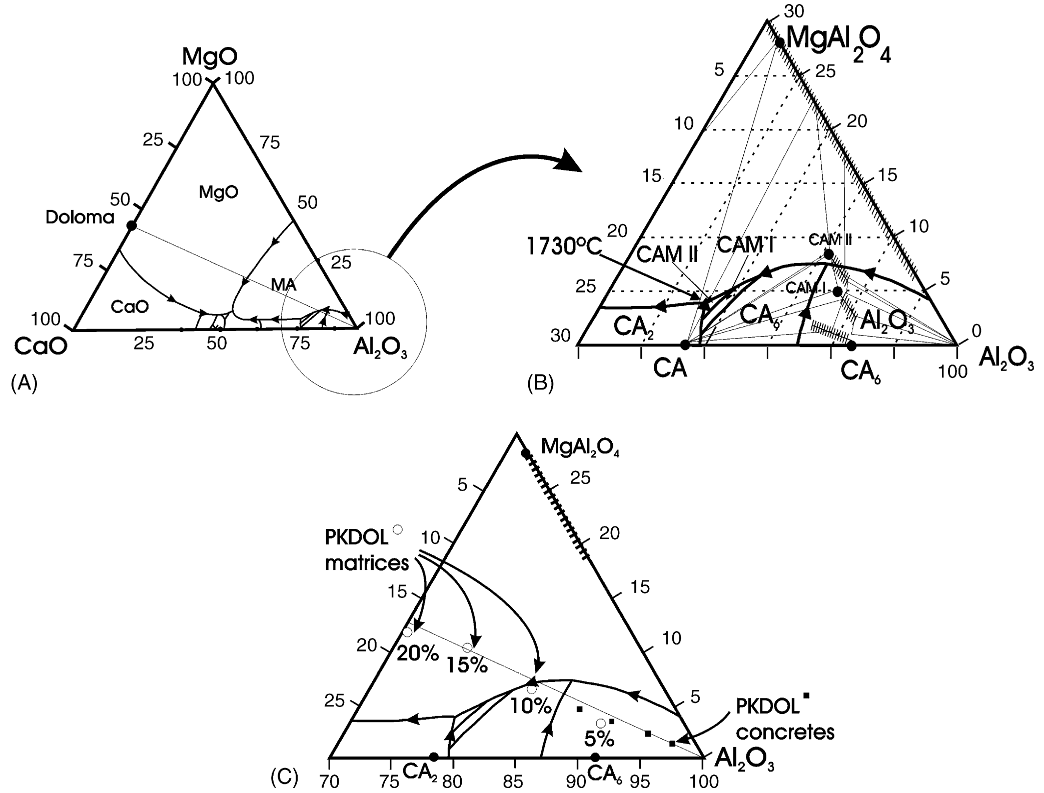

Fig. 1. (A) Al_2O_3–MgO–CaO ternary phase equilibrium diagram (after de Aza et al.[16]); (B) isothermal section at 1650 °C of the Al_2O_3-rich zone; (C) theoretical position of the PKDOL concretes and their corresponding matrices in the Al_2O_3-rich zone.

composition of a given granulometric fraction (<125 μm) and the total concrete granulometric curve (based on Andreassen's equation) by taking into account the percentages and the chemical composition of the selected raw materials. Fig. 1 shows the location of the matrix and refractory compositions on the doloma-alumina straight line in the Al_2O_3–MgO–CaO ternary diagram. Table 1 shows the matrix and refractory compositions of the three main oxides as well as the granulometry and the amount of each raw material used in the preparation of the four refractory castable compositions. The calcium aluminate cement content was 2 wt.% for the PKDOL5% and 10% compositions and 1.5 wt.% for the PKDOL15% and 20% compositions. Details about sample compositions can be found elsewere.[13,14] Cylindrical samples (40 mm height, 30 mm outer diameter and 10 mm inner hole diameter) were obtained by mixing matrix powders with 1.87–2.1 wt.% water. The samples were cured

Table 1
Theoretical chemical composition (wt.%) of the matrices (fraction < 125 μm) of the different refractory castables

	Grain size	Refractory castable compositions			
		PKDOL5%	PKDOL10%	PKDOL15%	PKDOL20%
Raw material					
T-60	−14 mesh, 6–10 mesh	31	31	31	31
Corundum	0–0.2 mm	40.34	40.34	41.34	41.34
CT9SG + CL370C	<125 mm	24.35	22.13	18.63	16.53
Dolomite	<125 mm	2.28	4.50	6.50	8.60
CA-270	<125 mm	2	2	1.5	1.5
Bulk compositions (wt.%)					
Al_2O_3		96.29	95.34	90.88	88.16
WlgO		1.30	2.54	3.65	4.80
CaO		2.41	4.12	5.47	7.04
Matrix compositions (wt.%)					
Al_2O_3		90.62	83.36	76.74	70.19
MgO		3.29	6.36	9.31	12.08
CaO		6.09	10.26	13.95	17.73

at room temperature in airtight containers for 24 h and subsequently dried at 110 °C for 24 h before firing. Creep tests were performed in an Instron testing machine (model 8562) coupled to an electric furnace. The specimens were heated up at a constant rate of 10 °C/min below 1000 °C and then at a heating rate of 5 °C/min to reach the final test temperature. The temperature was maintained for 30 min before testing, and then a fixed load of 2 MPa was applied. Displacement due to deformation under load versus temperature was recorded.

Samples taken from matrix materials fired in the temperature range 400–1500 °C were crushed and sieved (<40 μm) for X-ray powder diffraction (XRD) analysis. The X-ray patterns were recorded on a Siemens D-5000, using Cu Kα radiation operating at 30 mA and 40 kV. X-ray diffraction powder patterns were carried out over the 2–65° (2θ). The semi-quantitative phase contents were determined using integrated XRD peak intensities. A microscopic examination was performed on the fired samples (matrix fracture surfaces) by scanning electron microscopy (SEM) (Zeiss, DSM 942-model) based on a Link Isis II energy dispersive spectroscopy (EDS) system. All the samples were Au coated in an Emscope SC 510 sputtering before their analysis by SEM.[1–3]

3. Results and discussion

3.1. Phase evolution

Fig. 2 shows the phase evolution of PKDOL5%, 10%, 15% and 20% matrices studied by XRD from room temperature to 1500 °C. At room temperature, alumina gel, hydrated calcium aluminates, dolomite, and Al_2O_3 phases co-exist. When the temperature increases the structure of the hydrates changes and dehydrated phases appear. At 600 °C the $C_{12}A_7$[d] phase is formed from the amorphous dehydrated calcium aluminates. At 800 °C, an increase in the crystallinity of the samples takes place. The CA[e] phase formed from the Al_2O_3 and $C_{12}A_7$ reaction can be observed from 800 °C onwards and reaches its maximum degree of recrystallisation at 1000 °C for all compositions except for PKDOL20% which presents this maximum at 1100 °C (Fig. 3). At higher temperatures the CA reacts with free Al_2O_3 to form CA_2.[f] This reaction presents a relative volume increase of 13.6%,[15] being absorbed by the material thanks to the presence of a viscous vitreous phase at this temperature (Fig. 4). A spinel phase is also detected by XRD. Spinel is formed by the reaction of free Al_2O_3 and the MgO coming from dolomite (Fig. 5). At 1300 °C the whole CA phase has already been dissolved and the CA_6,[g] resulting from the $CA_2 + Al_2O_3$ reaction, has not yet been formed. At 1400 °C CA_6 has been formed, exhibiting a platelet morphology (Fig. 6). These crystals form a network of interlocked platelets transfixing the alumina grains.

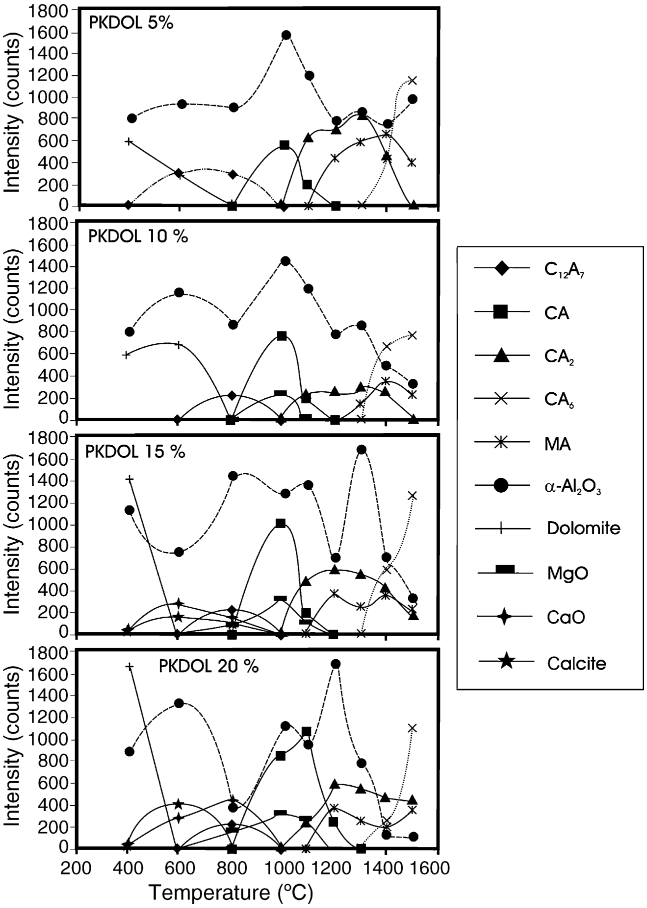

Fig. 2. Phase evolution of the PKDOL5%, 10%, 15% and 20% matrices from 400 to 1500 °C.

3.2. Deformation curves

Fig. 7 shows the curves deformation–time at different temperatures in the range 1100–1400 °C for all the matrices. All the materials present an important deformation rate during the first stage of creep. From 1300 °C onwards the total deformation exceeds 12% during the first 2 h. But at 1100 and 1200 °C an

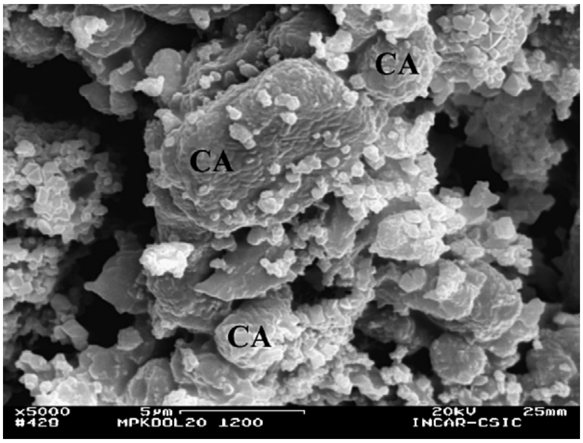

Fig. 3. CA crystals in a PKDOL20% matrix at 1200 °C.

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[d] Chemical formula: $12CaO{\cdot}7Al_2O_3 = C_{12}A_7$.

[e] Chemical formula: $CaO{\cdot}Al_2O_3 = CA$.

[f] Chemical formula: $CaO{\cdot}2Al_2O_3 = CA_2$.

[g] Chemical formula: $CaO{\cdot}6Al_2O_3 = CA_6$.

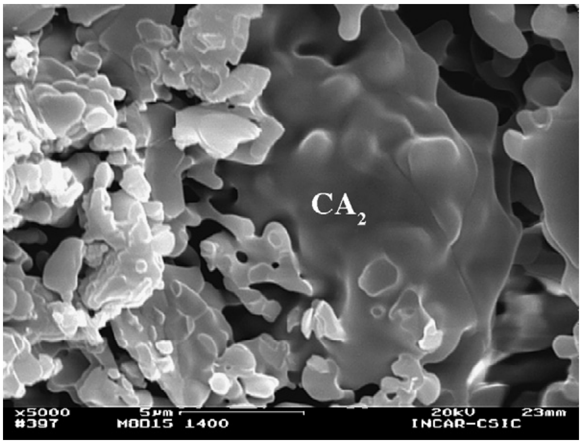

Fig. 4. Vitreous phase surrounding CA_2 crystals at 1400 °C.

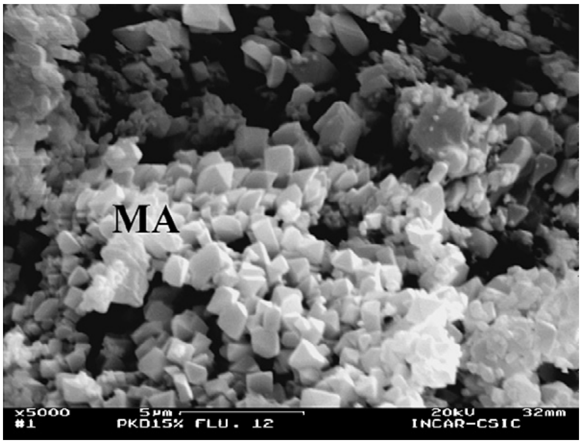

Fig. 5. Spinel crystals (MA) in a PKDOL15% matrix at 1200 °C.

important deceleration of creep rate takes place reaching a clear secondary steady stage with a constant creep rate.

The high deformation rate observed during the first stage of primary creep is related to the important microstructural changes taking place in the matrices at low temperatures. Above 1000 °C, the reaction $CA + A \rightarrow CA_2$ takes place in the presence of an important amount of glassy phase which is the fundamental mechanism governing the deformation in this region. In fact, PKDOL15% and 20% compositions present a greater deformation at 1100 °C than at 1200 °C, confirming the influence of the previous reaction. When this reaction is completed (at 1200 °C for all compositions except PKDOL20% which concludes at 1400 °C) the materials present the same deformation rate regardless the quantity of added dolomite. To confirm this hypothesis several specimens of the PKDOL15% matrix were prepared according to the conditions presented in Table 2 in order to obtain materials with a different degree of microstructural evolution by using different holding times at 1100 °C (30 min, 2.5 and 5 h). These specimens were subjected to creep tests. Fig. 8 shows the deformation curves under load for the different PKDOL15% treated specimens. A cross-section of creep specimens number 4

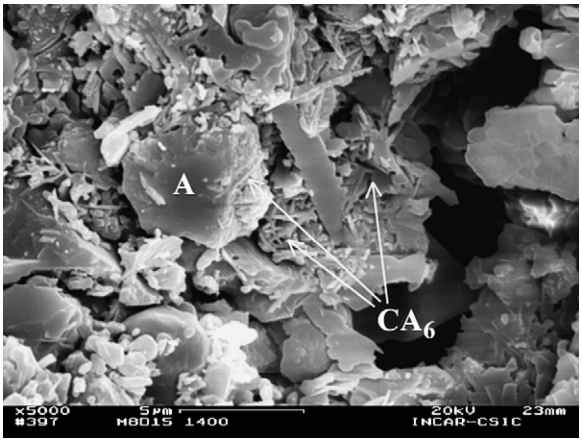

Fig. 6. CA_6 crystals at 1400 °C with a high aspect ratio, transfixing the alumina grains (A).

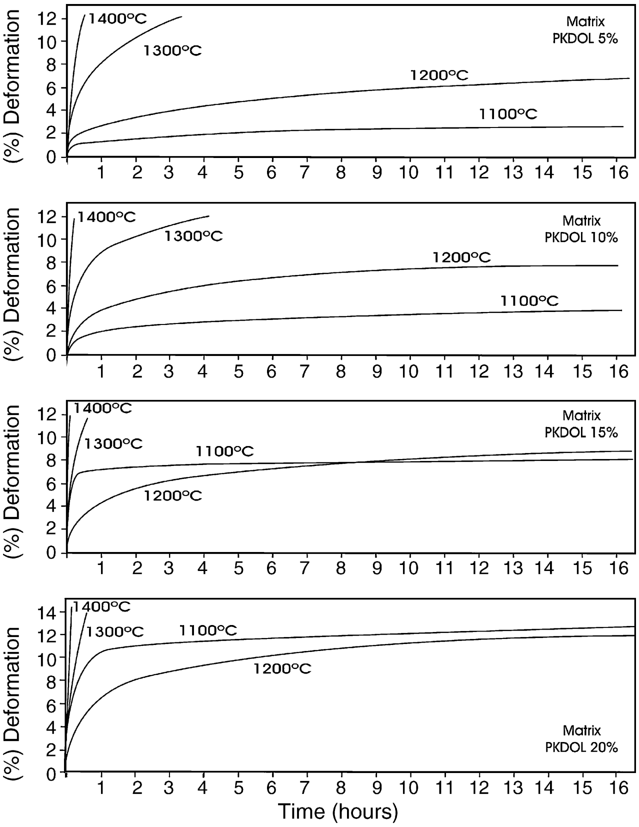

Fig. 7. Creep curves of the PKDOL5%, 10%, 15% and 20% matrices in the temperature range 1100–1400 °C.

Table 2
Test conditions of the PKDOL15% matrix specimens

Sample number PKDOL15%	Testing conditions		
	Maximum temperature (°C)	Time	Applied load
1	1100	Quenched	No
2	1100	30 min	No
3	1100	12 h	No
4	1100	30 min	2 MPa, 20 h
5	1100	2.5 h	2 MPa, 20 h
6	1100	5 h	2 MPa, 20 h

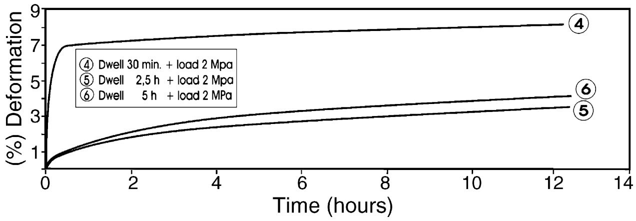

Fig. 8. Creep curves of the PKDOL15% matrices after different thermal treatments.

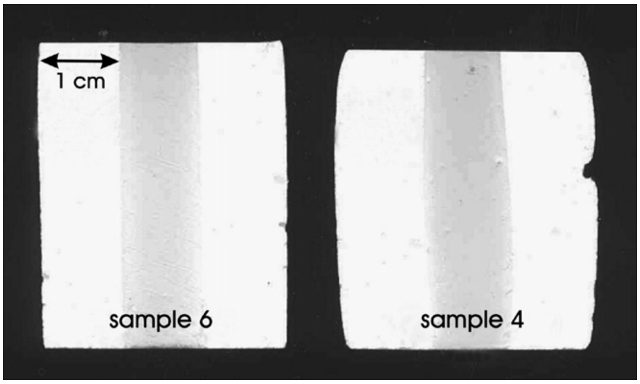

Fig. 9. Creep sample numbers 4 and 6 (Table 2).

(30 min at 1100 °C) and 6 (5 h at 1100 °C) is provided in Fig. 9. Sample 4 shows an important final deformation after 20 h of creep test compared to sample 6. It is clear from Fig. 8 that the final deformation at 1100 °C seems to depend to a large extent on the stabilization of the microstructure at 1100 °C. In other words, it depends on the evolution of the reaction between CA and A to form CA_2. A period of time shorter than 30 min implies a very high deformation during the first region of primary creep. Then suddenly a slow-motion deformation starts until the secondary stage of creep is reached. However, if the specimens are subjected to a longer thermal treatment (more than 1 or 2 h) before the load is applied, a notable reduction in the primary stage of deformation occurs.

Table 3 shows the phases studied by XRD of specimens 1 to 6. This table confirms the fact that $CA + A \rightarrow CA_2$ is the fundamental reaction governing the deformation in the first region of primary creep. Only specimens 1 and 2 (quenched) possess the CA phase in their microstructure. Sample 2 with a dwelling time of 30 min at 1100 °C starts to show a small amount of CA_2 phase due to the $CA + A \rightarrow CA_2$ reaction. When loading the sample at 2 MPa an important deformation (7%) takes place during the first 30 min of test (specimen 4). Once the $CA + A \rightarrow CA_2$ reaction has taken place, a dramatic reduction in the deformation rate occurs and the samples show a completely different behaviour. $CA + A \rightarrow CA_2$ is a reaction produced in the presence of a transitory vitreous phase and depending on the kinetics of the reaction, the refractory castable will show greater or lesser deformation rate with time (Fig. 10).

Table 3
Phase evolution of the PKDOL15% specimens after different test conditions (Table 2)

Phases	1	2	3	4	5	6
Al_2O_3, corunduin	–[a]	–[a]	–[a]	–[a]	–[a]	–[a]
CA	–[b]	–[b]				
CA_2		–[b]	–[b]	–[b]	–[b]	–[b]
$C_{12}A_7$, mayenite	Traces					
MgO, periclase	–[c]	–[b]	Traces			Traces
$MgAl_2O_3$, spinel			–[b]	–[b]	–[b]	–[b]

[a] High.
[b] Medium.
[c] Low.

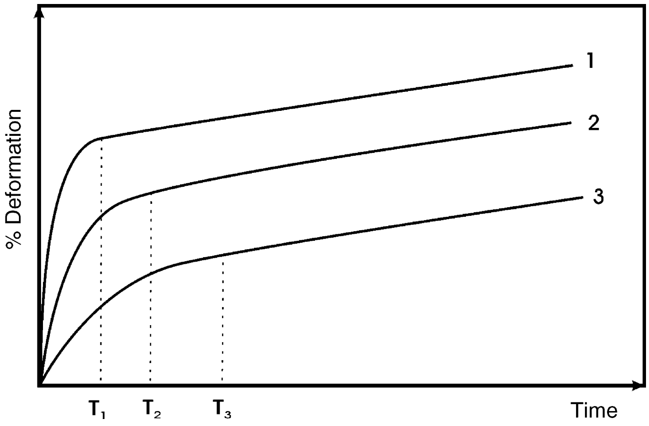

Fig. 10. Theoretical deformation curves of materials with different $CA + A \rightarrow CA_2$ reaction progress.

4. Conclusions

Based on the results of the present investigation the following conclusions can be drawn:

(1) The reaction $CA + A \rightarrow CA_2$ is a fundamental reaction taking place in the microstructural evolution with temperature in high alumina concretes with dolomite additions. This reaction starts at about 1000 °C and is produced in the presence of an amorphous phase. Depending on the stage of the reaction there will be a greater or lesser deformation with respect to time.
(2) In the temperature interval ranging from 1100 to 1200 °C, the creep resistance of refractory castables with dolomite additions hardly depend on its thermal history, that is the microstructure developed as a consequence of the reaction $CA + A \rightarrow CA_2$.
(3) At 1300 °C all the CA phase has already been dissolved and the CA_6, resulting from the $CA_2 + A$ reaction, has not yet been formed. At this temperature, the refractory castables exhibit the worst operating conditions with high deformation rates.

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