Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 3383–3389

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

The effect of sintering behaviour and phase transformations on strength and thermal conductivity of disposable tundish linings with varying compositions

A.R. Pal [a,*], S. Bharati [a], N.V.S. Krishna [a], G.C. Das [b], P.G. Pal [c]

[a] *Refractory Technology Group, Tata Steel Ltd., Jamshedpur, India*
[b] *Dept of Metallurgical Engineering, Jadavpur University, Kolkata, India*
[c] *Govt. College of Engineering and Ceramic Technology, Kolkata, India*

Received 1 October 2011; received in revised form 19 December 2011; accepted 19 December 2011
Available online 28 December 2011

Abstract

The durability of insulating tundish linings depends on the sintering characteristics of the mix formulation and its ability to restrict corrosion. The present work studied the effect of mix variations on the performance of tundish working lining material. This was evaluated in terms of bond formation, strength and thermal conductivity of the lining material. In the present study, a siliceous olivine-periclase and a low silica magnesia based compositions were investigated. The samples evaluated were heat treated at 250–1450 °C for 2 h. Microstructure of the heat treated samples was analysed by QEM SCAN and SEM. A solid-state sintering by formation of high refractory phases like forsterite and magnesio-wustatite at the interface of the grains is believed to have enhanced the high temperature strength of olivine based recipe. In contrast, liquid phase sintering was predominant in periclase based formulation, imparting a lower strength at high temperature. The sintering behaviour of the mixes was also found to have a profound effect on thermal conductivity of the two materials.

Keywords: C. Thermal conductivity; Tundish disposable lining; Olivine; Forsterite; Wustite

1. Introduction

Despite the known problems existing in refractories for continuous casting, a continual push exists to improve steelmaking efficiency due to international competition, which has driven the need for process improvements. The search for new refractory materials to improve their performance is a priority as steel manufacturers want increased service and equipment life. Special attention has been devoted not only to the quality and elevated endurance of refractory lining, but to the effectiveness of the new technology and new materials.

Given the drive to improve steel quality, several developments have been made in the continuous casting area, including adopting disposable lining to protect the permanent refractory lining of the tundish. These expendable liners are usually fabricated from a composition having heat insulating properties either in the form of boards or sprayable materials. Recently, the technology in disposable linings has shifted from boards or sprayable materials to dry vibratable material (DVM) premixed with a binder and used to obtain a disposable layer over the permanent lining [1]. Typically, the dry refractory material is cured with heat prior to use so as to obtain the disposable working lining.

In continuous casting of steel, a break in production is very common due to the poor performance of disposable lining. In practice, it has been observed that the failure of disposable lining depends not only on corrosion, but also on erosion of the refractory material. Until now, corrosion of working lining by steel slag has been the focus of many investigations [2–5]. Very little research, however, has been reported on the strength of the working lining material at operating temperature [6,7]. Poor mechanical strength is one of the known causes dislodging refractory grain from a matrix, leading to lining erosion. Since the actual cause of refractory failure is a combination of both corrosion and erosion, it is important that the mechanism of

---

* Corresponding author. Tel.: +91 657 6648901.
E-mail address: atanu1@tatasteel.com (A.R. Pal).

0272-8842/$36.00 © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2011.12.049

strength development in a disposable material be better understood.

Thermal conductivity of the disposable liner is another area of concern. During prolonged casting, the disposable lining must act as a thermal barrier layer, protecting the permanent liner, and maintaining the temperature of the molten steel. If the disposable liner has a high thermal conductivity, it can react with and fuse to the permanent lining at elevated temperatures. As a result, deskulling of the disposable liner becomes difficult, and the permanent lining can become damaged during the deskulling process.

A number of various dry refractory materials with varying compositions are available in industry; however, the most commonly used material is made of forsteritic olivine ($MgFeSiO_4$) with periclase (MgO) [8]. These mixtures supply low conductivity and are compatible with steel de-oxidation products like FeO and MnO. Still, there is a need to bridge the gap in understanding various properties of these working lining materials that is necessary in the selection of high performing linings. Further, pure MgO is widely used in steelmaking refractories because of its superior slag corrosion resistance. In our earlier studies, disposable lining materials based on pure periclase system showed better slag corrosion resistance compared to periclase-olivine based DVMs [2]. Hence, efforts have been made to explore the suitability of using only periclase system as tundish disposable lining in terms of mechanical and thermal properties. The present study also explores the sintering aspect of a commonly used periclase-olivine based DVM for tundish working lining to understand and correlate the effectiveness of bond formation on the prospective strength and thermal conductivity properties.

2. Materials and methods

In this context, the DVM considered is a commonly used one with DBM:olivine in the ratio of approximately 40:60. Chemical compositions of the above refractory components are given in Table 1. PO is used to denote the material consisting of periclase and forsteritic olivine, whereas P is used to indicate the DBM based dry mix considered for this study. Phenol formaldehyde based resin has been used as the green binder system for both the mixes. Grain size for mix PO was in the range of 0–1 mm whereas that for mix P was 0–3 mm. Typical composition and grain size distribution of the two mixes are shown in Tables 2 and 3 respectively. Screen analysis was done using Tyler sieves. As per the understanding from our earlier study, the presence of larger grains in a periclase based dry mix makes it more resistant to slag corrosion than a periclase-olivine mix with smaller grains [2]. Hence, without changing the grain sizing, the above two mixes have been considered to evaluate their other thermo-mechanical properties. The effect of particle size distribution on various properties, however, has not been considered in the present study.

Table 1
Chemical composition of the refractory components used in DVM PO (wt%).

	CaO	SiO_2	MgO	Fe_2O_3
DBM	<0.5	1.5–3	93.0	<1
Olivine	<0.5	35–45	45–50	8–10

Table 2
Typical chemical composition of the mix formulations (wt%).

	CaO	SiO_2	MgO	Fe_2O_3
PO	0.5	23.04	61.5	4.13
P	1.78	3.32	92.81	0.6

Table 3
Grain size distribution of mixes PO and P (wt%).

Grain Size (mm)	PO	P
>2.360	NIL	20–25
>0.850	4–6	20-25
>0.425	25–30	4–6
>0.250	20–25	8–10
>0.150	20–25	4–6
>0.106	10–12	4–6
>0.075	7–10	1–5
<0.075	NIL	20–25

Test samples of the above mixes were prepared by taking the dry mix in moulds of required sizes and vibrating for 10 s at a frequency of 50 Hz. The blocks were initially heated at 250 °C for 2 h to obtain handling strength, followed by heating to 1450 °C, where materials were held for 2 h to develop ceramic bonding.

Chemical analyses of the samples were determined by inductively coupled plasma (ICP, Model No. – ARCOS-165). The effect of sintering temperatures on the extent of bond formation was studied by measuring cold crushing strength (CCS) of the two materials at a constant load rate (Chemino, Model No. – CCS 26/501) as per ISO 10059-2:2003(E).

Microstructural studies were conducted on both samples after heating to 250 °C and 1450 °C using a scanning electron microscope (SEM – JEOL, Model JXA-6400) under back scattered energy (BSE) mode. Elemental analysis of the microstructure was conducted using energy dispersive spectrometer (EDS) coupled with the SEM.

The effect of heat treatment on the fraction of different phases formed at 250 °C and 1450 °C was analysed using quantitative evaluation of minerals software on a scanning electron microscopy (QEMSCAN) instrument (Model No. E430). QEMSCAN uses electron beam technology combined with high resolution BSE (back scattered electron) and SE (secondary electron) imaging having up to four light element energy dispersive spectrometers (EDS), and a microanalyser to analyse minerals. During QEMSCAN analysis, a detailed database of statistically representative mineral particle information is built up, which are later interrogated by the user. It is a powerful automated system that can acquire and process vast amounts of chemical and surface data.

Thermal conductivity of a material is dependent on the starting material and the microstructure that develops in it. The effect of starting material on thermal conductivity of the

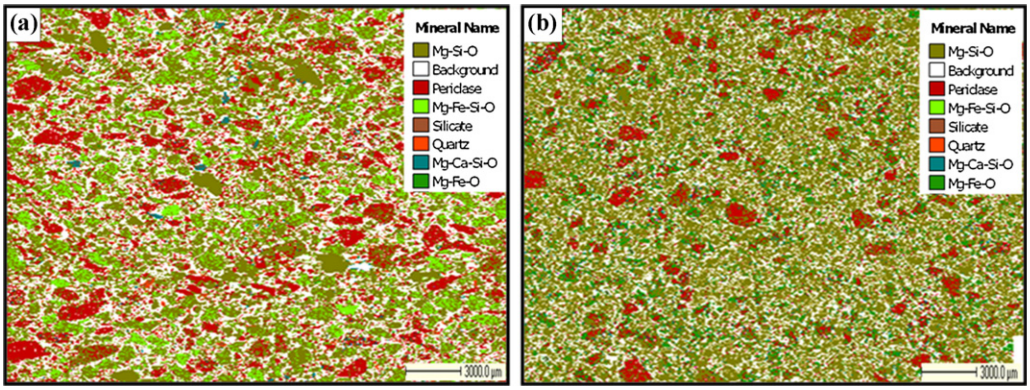

Fig. 1. QEMSCAN photo of sample PO after heat treatment at (a) 250 °C and (b) 1450 °C.

material at different temperatures was evaluated using calorimetric technique (Chemicals & Instruments Corporation, Kolkata) per standard IS:9490-1980.

3. Results and discussion

3.1. QEMSCAN study

Mineral phase change and their relative quantities after sintering for both mixes are shown in Figs. 1–3. Fig. 1(a) and (b) shows QEMSCAN imaging of olivine based mix PO after heat treatment at 250 °C and 1450 °C respectively. From the colour difference, it is noted that a decrease in periclase content (dark red) from 250 °C to 1450 °C occurs with a simultaneous increase in forsterite (Mg_2SiO_4) content (dark green) in the material. Phases such as quartz (SiO_2), considered during analysis, were found to be absent in the mix PO. However, not much of a difference could be observed in the case of mix P before and after heat treatment (Fig. 2(a) and (b)), which indicates that the phases present may not be reacting.

The presence of olivine in the PO material makes it more reactive during sintering at higher temperatures. This is evident from the quantified phase changes as shown in Fig. 3(a) after heat treatment at 1450 °C. There is a decrease of approximately 6% in the Mg–Fe–Si–O based phase and a similar increase of forsterite. Further, there is an appearance of magnesio–wustite (MgO–FeO), a new phase which is formed by the dissolution of FeO into periclase grains. The above facts, along with a

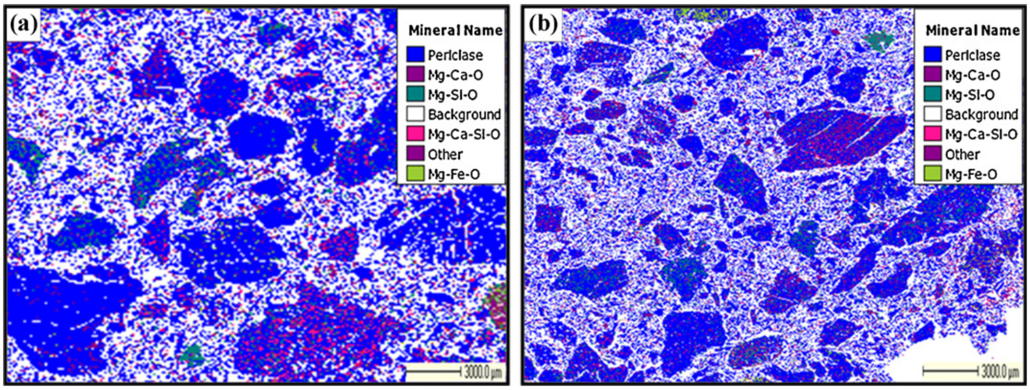

Fig. 2. QEMSCAN photo of sample P after heat treatment at (a) 250 °C and (b) 1450 °C.

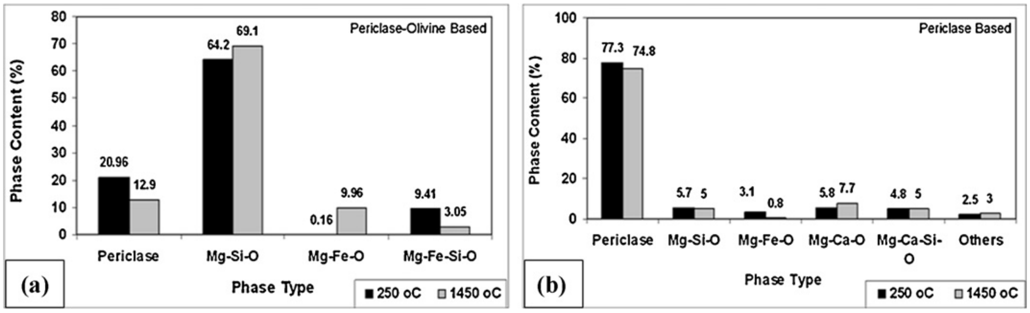

Fig. 3. QEMSCAN quantitative estimation of phase changes after heating at 250 °C and 1450 °C (a) mix PO and (b) mix P.

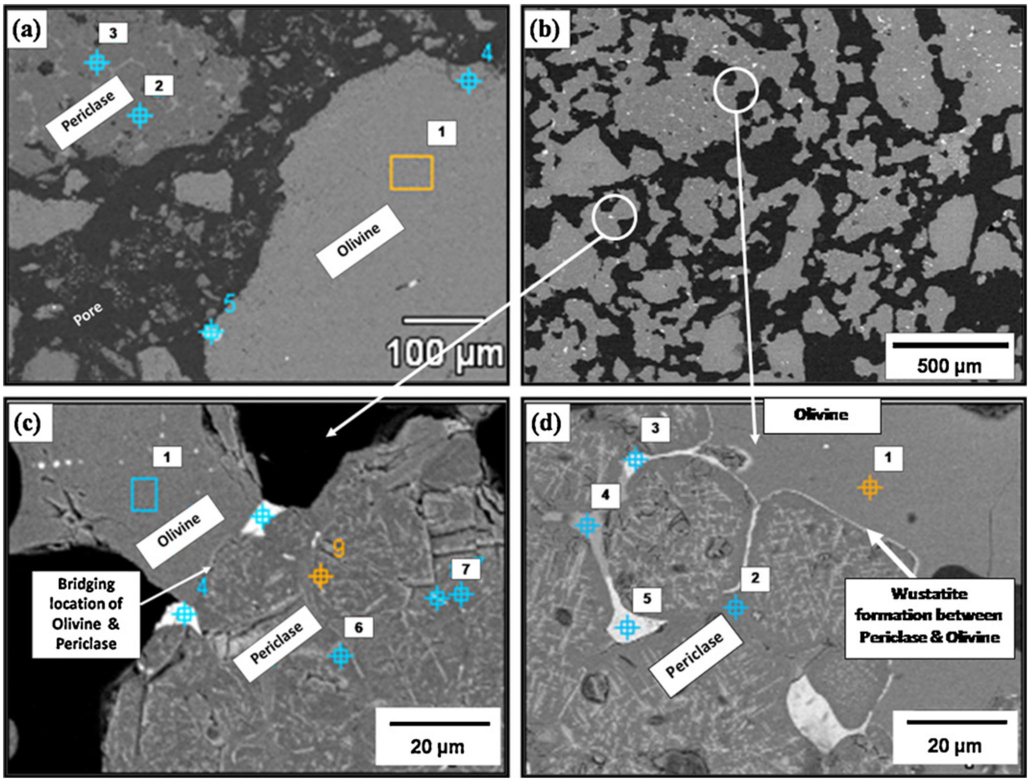

Fig. 4. Change in phase observed in mix PO (a) before and (b) after heating at 1450 °C, (c) and (d) micrographs at higher magnification.

decrease in periclase content in the system by approximately 8% are indicative of the dissociation of Mg–Fe–Si–O phase to form forsterite and wustite when reacting with periclase at high temperature. On the contrary, from the quantified phase changes as shown in Fig. 3(b), the periclase based material is observed to be relatively stable at high temperature.

3.2. SEM study

The microstructural analyses of both mixes are shown in Figs. 4 and 5. Figs. 4(b) and 5(a) show the sintering behaviour of samples PO and P respectively at 1450 °C at low magnification. A clear matrix interlinking could be seen in both the samples. Also liquid phases formed by silicate impurities present in DBM in mix P appear prominently bright at the intergrain boundaries and their absence is typical in sample PO. When observed at higher magnification, the details of grain to grain bonding mechanisms became evident in mixes PO and P (Figs. 4c and d and 5b).

Fig. 4a shows the SEM micrograph of mix PO prior to sintering, with an elemental analysis listed in Table 4. FeO content of the olivine grain was found to be approximately 8% whereas that present in periclase grains is $<1\%$. When heated to a temperature of 1450 °C, two types of bonding mechanism between periclase and olivine grains were observed. Fig. 4(c) shows a direct bonding between the grains by forming a forsterite solid solution at the contact point near interface. In addition, a solid solution between MgO from periclase and FeO from olivine was also found to coexist between periclase and olivine grains by forming wustite (Fig. 4(d)), thereby bridging

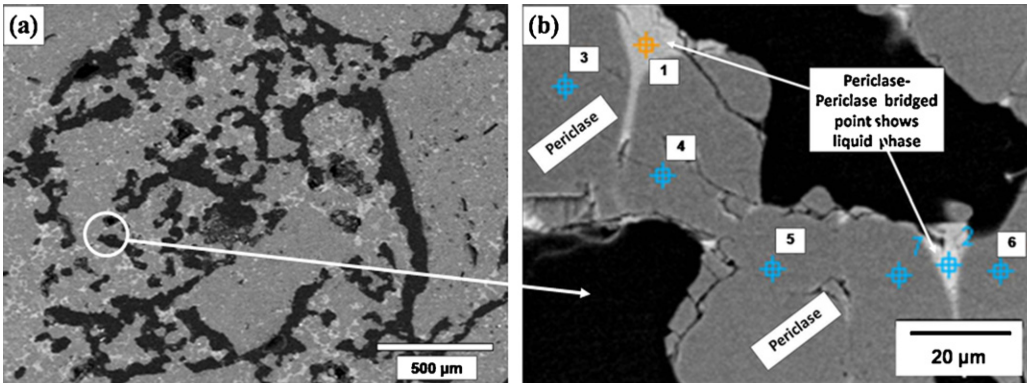

Fig. 5. Change in phase observed in mix P after heating at 1450 °C, (a) low magnification and (b) high magnification.

Table 4
EDS analysis of Fig. 4a (wt%).

Point	MgO	SiO_2	CaO	FeO	Phase
1	48.10	43.65	0.00	8.25	Olivine
2	99.24	0.00	0.00	0.76	Periclase
3	29.93	41.16	28.91	0.00	Monticellite

Table 5
EDS analysis of Fig. 4c (wt%).

Point	MgO	SiO_2	CaO	FeO	Phase
1	53.49	44.75	0.00	1.76	Forsteritic Olivine
6	95.96	0.00	0.00	4.04	Periclase
7	95.03	0.00	0.00	4.97	-do-

the two grains. An increase in fosterite as well as wustite content is expected to enhance more solid–solid bonding in olivine based materials. Further, visible exsolutions in periclase grains and their absence in adjoining olivine grains could also be seen, clearly indicating Fe ion diffusion into periclase grains from olivine. This is a typical phenomenon in periclase–olivine system, with the extent of diffusion also confirmed from the EDS analysis (Tables 5 and 6). This indicates that magnesio–wustite formation is thermodynamically favored compared to a fayalite (Fe_2SiO_4)–fosterite solid solution. An increase in fosterite content of the olivine phase in sample PO, as explained based on QEMSCAN results (Fig. 1), is possible only when there is inter diffusion of Fe and Mg ions.

In contrast, the formation of a liquid phase in sample P seemed to have facilitated the sintering process. The periclase grains are relatively pure, and a liquid forming monticellite ($CaMgSiO_4$) phase is found only at the contact area between large grains and the fine matrix (Fig. 5(b)), with its distribution favorably discontinuous. Utilizing EDS technique yielded the results shown in Table 7.

Sintering of the refractory is important to improve the mechanical strength of a working lining. Thermo-chemical changes like grain bridging on heat-treatment varies with the composition of the used mixes, as observed in Figs. 4 and 5. Formation of a solid solution due to interdiffusion at the periclase-olivine grain contact point in sample PO is expected to have enhanced solid–solid sintering. Bygden [9] reported similar inter diffusion of Fe–Mg ions resulting in periclase–wustite bond formation in a static corrosion study of MgO samples in contact with FeO–CaO–SiO_2 slags. In addition, the extent of grain to grain contact in such types of solid–solid sintered materials is more compared to pure periclase systems. Hence, the presence of iron oxide as an impurity in forsteritic olivine based mixes causes an improved bonding in the composition. In contrast, the amount of liquid phase formed in mix P, was found to be less and discontinuous, which might be due to the use of highly pure periclase grains. The presence of such liquid phases at the grain interfaces restricts direct bonding between the grains, something that would cause lower strength. During service in tundish applications where working lining temperature can vary from 1450–1600 °C, the solid–solid bonded forsterite rich composition would be expected to have strength advantages over liquid phase bonding existing in pure MgO based materials.

Table 6
EDS analysis of Fig. 4d (wt%).

Point	MgO	SiO_2	FeO	Phase
1	53.43	44.27	1.82	Forsteritic Olivine
2	98.28	0.67	1.04	Periclase
4	64.34	0.00	35.66	Wustite

Table 7
EDS analysis of points in Fig. 5b of mix P after sintering (wt%).

Point	MgO	SiO_2	CaO	Phase
1	29.82	42.10	28.08	Monticellite
3	100.00	0.00	0.00	Periclase
4	100.00	0.00	0.00	-do-
5	100.00	0.00	0.00	-do-
6	99.63	0.00	0.00	-do-

Further, it has been reported that olivine, when heated in the presence of oxygen, dissociates to forsterite or ferriolivine, depending on the composition [10]. The olivine used for the present work is richer in forsterite (Mg-end member) than fayalite (Fe-end member). When heated at high temperature, the olivine in mix PO dissociated to the high temperature phase forsterite (melting temperature about 1900 °C), with no fayalite formation. The absence of the low temperature phase fayalite (melting temperature of approximately 1220 °C), is expected to have a significant effect on the high temperature strength of mix PO.

3.3. CCS study

CCS of the refractory blocks was measured at room temperature after firing at six temperatures (250 °C, 600 °C, 1000 °C, 1150 °C, 1300 °C and 1450 °C) for 2 h (Fig. 6). The higher strength at 250 °C is a result of the resin binder used to bond the dry mixes. The higher strength of mix P compared to that of PO can be attributed to larger DBM grain sizes present in P. However, as the temperature was increased to 600 °C, the

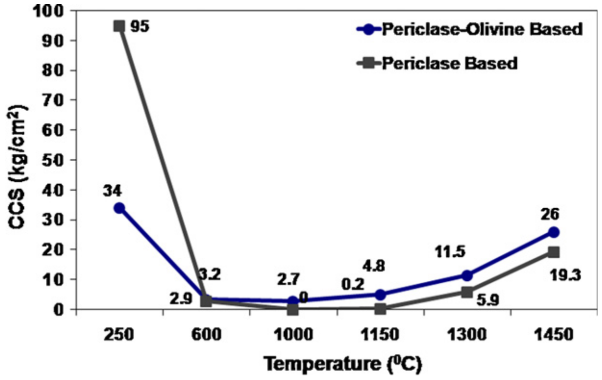

Fig. 6. CCS of samples obtained from mixes PO and P at different temperatures.

resin binder oxidised resulting in lower strength. Low strength in both mixes persisted up to 1000 °C because mixes had not started to develop a ceramic bond. However, when the temperature was increased further, sintering started to occur, causing an increase in strength. Less liquid phase that was discontinuous developed along the grain boundaries in mix P and is believed to have played a role in its low strength compared to mix PO, where the sintering was thought to be mainly solid–solid. In practice, the working lining materials are designed to have a low strength in the range of 800–1000 °C causing formation of a weak zone between the back-up castable lining and the working lining. The weaker the strength in that zone, the easier it is to deskull the tundish. In addition, the material is expected to develop sufficient strength at the operating temperature to withstand the ferrostatic pressure without causing any dislodging of the lining during casting.

3.4. Thermal conductivity

The measured thermal conductivity of mixes PO and P at temperatures 200 °C, 600 °C and 1000 °C respectively is shown in Fig. 7. It can be seen that periclase (P) has the highest thermal conductivity between the two, which is in agreement with reported values [11]. However, the addition of olivine to periclase brings down the thermal conductivity drastically, which is a desirable property in disposable linings.

The thermal conductivity of refractories is known to be dependent upon chemical and mineralogical compositions as well as the glassy phase contained in the refractory and the application temperature. The manner in which thermal conductivity of refractories varies with temperature depends on the nature of the material under investigation. One way of heat transfer through a solid occurs via energy transfer between vibrating atoms. At low temperatures (up to about 400 °C), energy travels through the material predominantly via lattice vibrations (phonons) at the speed of sound [12]. Lattice vibrations increase in frequency and amplitude as temperature increases until they are scattered, either through phonon–phonon interactions or at lattice imperfections. In general, phonon conductivity decreases with increasing temperature in crystalline materials as the amount of scattering increases. As it can be seen in Fig. 7, the thermal conductivity of both P and PO mixes increased with temperature. At higher temperatures, photon conductivity (radiation) becomes the predominant mechanism of energy transfer. This is a rapid sequence of absorptions and emissions of photons that travel at the speed of light. This mode of conduction is especially important in porous ceramics like the above mixes. The presence of multiple phases in mix PO, however, disrupts the heat flow to a greater extent due to different coefficients of thermal expansions, thereby resulting in lower thermal conductivity than mix P [12].

Considering the results obtained from the present work, it could be said that although the phases of periclase based material showed a stable behaviour at high temperature, the presence of direct bonding and grain-to-grain contact in the periclase-olivine based material would have a profound effect on the strength and thermal conductivity at the working temperature.

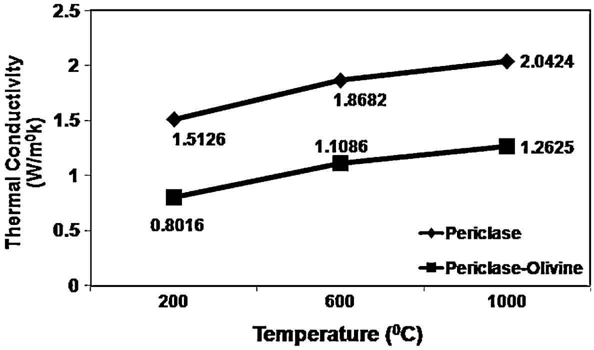

Fig. 7. Thermal conductivity of PO and P at different temperatures.

4. Conclusions

The suitability of both periclase and periclase-olivine based refractory compositions have been considered as tundish disposable liners. In spite of its very good corrosion resistance property as observed in our earlier studies, pure periclase based material may not work well in tundish linings due to their high thermal conductivity and poor sinterability to develop high temperature strength. Solid–solid bonding taking place in the periclase-olivine based mix formulation vs pure periclase based mix resulted in strength and thermal conductivity desirable for tundish applications. Further studies, however, are essential on binder selection, grain sizing and pore forming additions to explore the suitability of pure DBM system as tundish disposable lining material.

Acknowledgement

The authors wish to thank Dr Tamal K Ghosh for the microstructural studies using SEM and QEMSCAN instruments.

References

[1] M.J. Bradley, Overview of tundish dry vibe technology, MPT International, 2008,, p. 70–72.

[2] A.R. Pal, S. Bharati, N.V.S. Krishna, G.C. Das, P.G. Pal, Study of penetration and corrosion of olivine–periclase and periclase based tundish DVMs by molten slag, Ironmaking and Steelmaking 38 (8) (2011) p602–p607.

[3] A. Pack, S. Hoernes, T. Walther, R. Bross, Behavior of basic refractories at high temperatures in steelmaking processes – thermodynamics and implications for the usability of olivine as refractory material, European Journal of Mineralogy 15 (1) (2003) 193–205.

[4] B.M. Mostaghioum, A. Monshi, Hot corrosion mechanism of tundish plaster with steel slags, Journal of Material Science 42 (2007) 6720–6728.

[5] H.B. Johnson, K.J. Saylor, A comparison of disposable magnetic tundish lining systems, ISS 73rd Steelmaking Conference, 1990.

[6] W. Wuhua, X. Wendong, G. Changhe, Effect of matrix composition of dry vibration material for tundish on its properties, Refractories 41 (2) (2007) 126–129.

[7] L. Fang, L. Kaiqi, W. Bingjun, L. Yongfeng, J. Chunhua, Properties of magnesia based dry vibration mixture containing forsterite for tundish, Journal of the Chinese Ceramic Society 37 (5) (2009) 846–850.

[8] L.M. Akselrod, V. Egorov, Z.E. Goryacheva, Mixture of a base composition: consumable lining of tundish ladles of continuous casting machines, Journal of Refractories and Industrial Ceramics 37 (3,4) (1996) 137–139.

[9] J. Bygden, T. Debroy, S. Seetharaman, Dissolution of MgO in stagnant CaO–FeO–SiO_2 slags, Ironmaking and Steelmaking 21 (1994) 318–323.

[10] R.N Khisina, A.D. Khramov, V.M. Kolosov, A.A. Klesehev, A. Lawrence Taylor, Formation of ferriolivine and magnesioferrite from Mg–Fe–Olivine: reactions and kinetics of oxidation, Physics and Chemistry of Minerals 22 (1995) 241–250.

[11] H.B. Johnson, Making the grade for tundish linings: a growth market for DBM, in: Conference on Industrial Minerals, 'MagMin 2005', Vienna, (2005), pp. 1–19.

[12] W.D. Kingery, H.K. Bowen, D.R. Uhlmann, Thermal properties, in: Introduction to Ceramics, 2nd ed., Wiley, Singapore, 1976, Chapter-12.