Effect of Increase in Basicity of Slag on the Corrosion of Tundish DVM

Mousom Bag, Ritwik Sarkar, Atanu R. Pal

In continuous casting of steel, tundish acts as an intermediate vessel between ladle and mould. In order to satisfy the requirement of metallurgical technology development such as clean steel making, high speed casting, lowering of non-metallic inclusion, it is necessary to develop high quality tundish refractory with long service life. The present work studies the effect of basicity of tundish slag on the corrosion properties of tundish working lining, namely DVM. Addition of magnesia was done to tundish slag to increase its basicity. Corrosion behavior was studied by means of penetration depth, chemical and phase analysis of the corroded portion of the DVM samples. Penetration depth was found to be reduced significantly above a basicity of 0,72.

1 Introduction

Tundish is the last metallurgical vessel through which molten steel flows before shaping in mould and onwards solidification [1]. During the transfer of metal through tundish, molten steel interacts with the refractories, slag, tundish covering powder and atmosphere. Thus the working lining refractories play the major role as the molten metal is in contact with it and has to face the severe thermal-mechanical-chemical environment; so the quality and performance of the working lining determines the tundish performance, operation and life.

Again to keep the pace with the technological up-gradation in metallurgical industries, such as clean steel making, high speed casting, lowering of non-metallic inclusion, etc, it is necessary to develop high quality tundish refractory with long service life.

Technological advancement in steel making technology, especially for the demand of cleaner and faster steel production, has changed the working lining concept of tundish [2]. Initially introduced low density tundish boards offered good thermal insulation with low refractory consumption but had the major disadvantages of manpower and time requirement for lining preparation. Development of spray masses was a breakthrough for avoiding these disadvantages of boards but quality of spray lining is dependent on the spraying skill and proper drying. Dry vibrating mass (DVM) based on phenolic resin was also developed parallelly but cost of binder system and associated health and safety issues limited its use. Recently developed resin free binder system for DVM has eliminated the health and safety issues and makes it ideal working lining for tundishes [3].

DVM is a MgO based free flowing dry basic mass, containing silica as the second major constituent and is applied by pouring/casting with vibration at dry condition. Absence of water in the material results in no direct bonding with the permanent lining thus ensures easy de-skulling and increases the tundish lining life. Also water free system eliminates the chance of hydrogen pick up by metal from vapor. Advantages like easier installation, less manpower requirement, short heating period, smooth surface finish resulting in lesser erosion, etc. makes DVM very popular. Reduction in installation time, pollutant emission and energy requirement were reported by the use of DVM [4].

Slag in tundish is the remnant slag that has carried over to tundish from ladle or formed on reaction during operation from tundish covering material, fluxing material, etc. The slag has some beneficial role too in providing thermal insulation to liquid steel, protecting liquid steel from oxidation and also absorbing non metallic inclusions. However chemical attack of slag remains the main mechanism of corrosion and wear of the refractories. Slag may cause the damage to the refractory in different ways, like, dissolution of refractory or any of its components, reaction with refractory and formation of new phase, penetration of slag or any of its constituents, etc. In all the different corrosion mechanisms, basicity gap between slag and refractory is most important.

In the present work, corrosion behavior of DVM refractory has been studied by varying the basicity of tundish slag, through addition of free MgO in slag upto 20 mass-%, using static cup method for corrosion. Slag containing DVM samples were fired between 1350–1450 °C and tested for slag

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Fig. 1 **Slag corroded DVM samples before and after cutting**

penetration depth, chemical analysis and phase analysis of the reacted portions.

2 Experimental

DVM and tundish slag (both from *Tata Iron & Steel Company*/IN) were first characterized for chemical analysis by X-ray fluorescence spectrometer (*ARL*/CH) and phase analysis by X-ray diffractometer (*Panalytical*/NL). Next DVM cubes were prepared of dimension 75 mm × 75 mm × 75 mm by pouring the DVM powder into lubricated mould and allowed to vibrate for three minutes using a table vibrator at 53,3–66,6 Hz and 0,5 mm amplitude.

DVM cubes were then cured at 300 °C for 3 h. After cooling the cubes were drilled centrally of 25 mm in diameter and 30 mm in depth.

Next 4 slag samples, namely A, B, C and D were prepared using original tundish slag and addition of 5, 10, 15 and 20 mass-% of MgO powder (>99 % pure, chemical grade) respectively. 20 g of MgO containing different slag samples were placed in the drilled holes of different DVM cubes and then fired (*Kanthal* furnace) at 1350, 1400 and 1450 °C for 1 h. After cooling the fired cubes were cut through a central plane containing the axis of the drilled hole. Penetration depth was measured using digital calipers from the cut samples in downward direction and an average of 5 readings was taken. Fig. 1 shows the slag containing fired DVM samples before and after cutting. Chemical and phase analysis different samples were done by collecting samples from the reacted portions only of the corroded DVM cubes. Each test result indicated in the study is an average of three individual samples.

3 Results and discussion

Chemical analysis of the slag and DVM samples are given in Tab. 1. From the analysis it is clear that CaO/SiO_2 is not the representative ratio of basicity of the materials, hence (C+M)/(S+A) is used for the calculation of basicity. Phase analysis of slag sample shows (Fig. 2 a) different silicate phases of basic oxides namely anorthite (A) and diopside (D) as the major phases with little wollastonite (W) phase. DVM shows (Fig. 2 b) periclase (P) as the major phase with little amount of forsterite (F) and olivine (O) phases.

3.1 Penetration depth study

Increasing amount of MgO content in slag increases its basicity. Addition of 5, 10, 15 and 20 mass-% of MgO changes the basicity of slag to 0,55, 0,64, 0,72 and 0,81 respectively. Fig. 3 shows the variation in penetration depth against basicity of slag at different temperatures. It was found that with the increase in basicity of slag, the penetration depth for all the temperatures is reduced. This is due to the reduction in basicity gap between the slag and DVM refractory thereby reducing the reaction between them. Also increase in basicity (MgO content) in slag decreases the viscosity of slag thereby reducing its flowability and penetration depth in refractory. The slope of

Tab. 1 **Chemical analysis of slag and DVM [%]**

Sample	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	Cr_2O_3	CaO	MgO	MnO	C/S	C+M/S+A
Slag	50,67	8,21	2,71	0,17	0,81	19,03	8,63	6,47	0,33	0,42
DVM	26,56	0,104	4,39	0,051	0,38	1,6	62,53	0,11	0,06	2,39

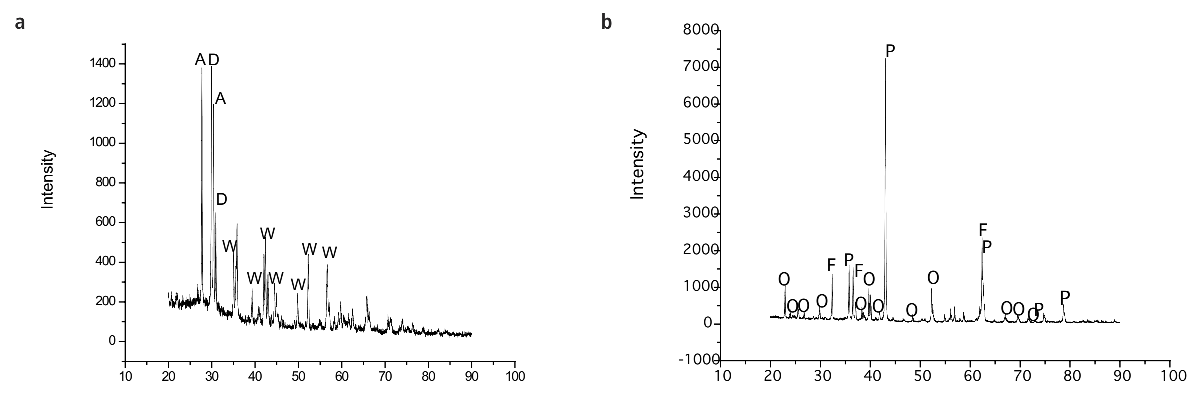

Fig. 2 **X-ray diffraction pattern of a) slag, and b) DVM, where A = anorthite, W = wollastonite, P = periclase, F = forsterite and O = olivine**

penetration depth has a distinct/sharp fall above the addition of 15 mass-% of MgO (basicity 0,72) for all the temperatures. Again, for any specific basicity of slag, increase in temperature increases the reaction rate and thus the penetration depth too. Viscosity of slag also decreases with increasing temperature thereby increasing the flowability of slag and resulting higher penetration depth.

3.2 Chemical analysis of the reacted portion

Reacted portion of the slag containing fired DVM samples are analyzed for oxide content and are represented in Tab. 2 – 4 for the 1350, 1400 and 1450 °C firings respectively. In general for all the temperatures, CaO and SiO_2 content was found to increase by about 2–3 mass-%, other components like MnO, Al_2O_3 were also found to be increased marginally whereas, MgO content was found to decrease in the reacted portion of the samples compared to that of the original DVM composition. It can be found that increase in the reaction temperature has nearly no effect on the compositional changes for most of the oxides, like CaO, SiO_2, MnO, Al_2O_3, Cr_2O_3 and TiO_2. An increase in the Fe_2O_3 content was also observed with increasing firing temperature to 1400 °C or above.

3.3 Phase analysis of the reacted portion

Phase analysis study of the reacted portion of the samples showed that periclase is the most strong and major peak for all the different samples and firing temperatures. Again, with the increase in the MgO content of slag, there are changes in the

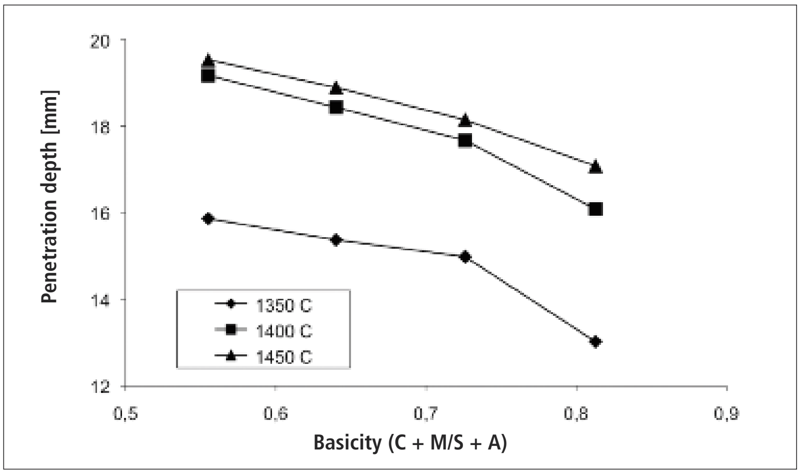

Fig. 3 Variation in penetration depth against basicity of slag

Tab. 2 Chemical analysis of the reacted part DVM fired at 1350 °C [%]

Sample	CaO	SiO_2	MgO	MnO	Al_2O_3	Fe_2O_3	TiO_2	Cr_2O_3
A	3,87	28,89	57,57	1,25	1,40	4,25	0,28	0,94
B	3,76	28,59	58,23	1,16	1,30	4,16	0,26	0,96
C	3,73	28,63	58,10	1,14	1,29	4,14	0,28	0,96
D	3,68	27,95	58,56	1,05	1,23	4,05	0,28	0,92

Tab. 3 Chemical analysis of the reacted part DVM fired at 1400 °C [%]

Sample	CaO	SiO_2	MgO	MnO	Al_2O_3	Fe_2O_3	TiO_2	Cr_2O_3
A	4,04	28,11	57,72	1,08	1,18	6,92	0,35	0,38
B	3,17	28,82	57,18	1,96	1,13	5,76	0,16	0,42
C	3,03	29,45	57,46	0,95	1,05	6,17	0,34	1,02
D	3,40	28,71	57,64	1,24	1,27	6,87	0,26	0,57

Tab. 4 Chemical analysis of the reacted part DVM at 1450 °C [%]

Sample	CaO	SiO_2	MgO	MnO	Al_2O_3	Fe_2O_3	TiO_2	Cr_2O_3
A	3,89	28,02	59,31	0,91	1,03	6,23	0,22	0,92
B	3,82	29,18	59,11	0,93	1,03	6,67	0,22	1,21
C	3,98	29,38	59,38	0,93	1,03	6,65	0,22	1,23
D	3,03	28,04	59,61	0,94	0,96	5,85	0,24	0,92

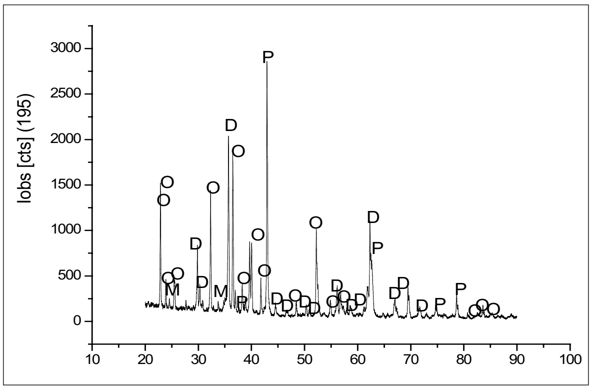

Fig. 4 X-ray diffraction pattern of the reacted portion of 1400 °C fired DVM sample containing slag A (5 % extra MgO)

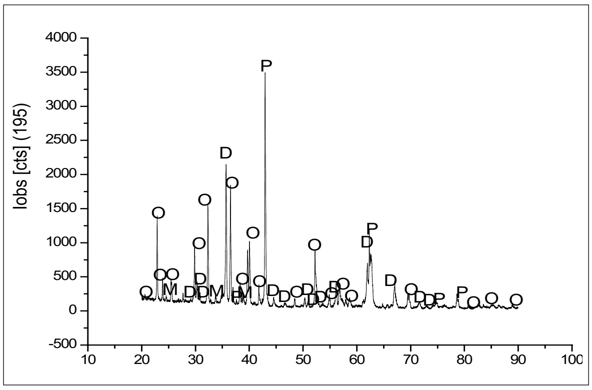

Fig. 5 X-ray diffraction pattern the reacted portion of 1400 °C fired DVM sample containing slag B (10 % extra MgO)

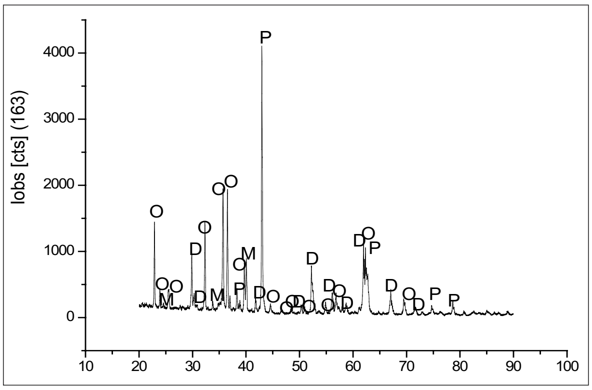

Fig. 6 X-ray diffraction pattern of the reacted portion of 1400 °C fired DVM sample containing C (15 % extra MgO)

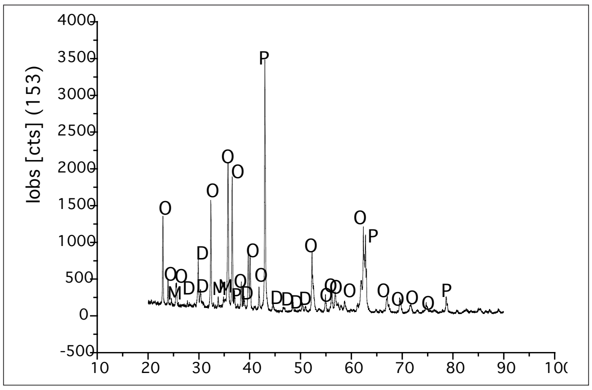

Fig. 7 X-ray diffraction pattern of the reacted portion of 1400 °C fired DVM sample containing D (20 % extra MgO)

minor/secondary phases of the samples. When 5 mass-% MgO is added to slag, the secondary phase is mainly diopside (D) ($CaMgSi_2O_4$) and olivine (O) [$(Mg.Fe)_2SiO_4$], but as the MgO content is increased in the slag the secondary phase is changing mainly to olivine and diopside phase intensity got reduced. Thus increase in basicity of the slag results in a higher MgO containing secondary phase, with higher temperature with-standability, indicating higher application temperature or better performance of the DVM. Also there is some presence of montecelite (M) ($CaMgSiO_4$). Fig. 4–7 show the XRD plots of the reacted portions of different compositions fired at 1400 °C, as a representative one.

4 Conclusion

Increase in basicity of slag was found to reduce the penetration depth for all the temperatures. Basicity above 0,72 shows significant reduction in penetration. Reacted portions of the DVM samples were found to have reduced MgO content and increased amount of CaO and SiO_2. Phase analysis shows that increase in basicity changes the secondary phase from diopside to olivine, in the reacted portions.

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