Development of Spalling-resistant Ladle Shroud and SEN with Carbon-free Inside Liner

Makoto NAKAMURA*1 Wei LIN*2
Masanori OGATA*3 Masato HASHIMOTO*4

Abstract

Ladle shrouds (LS) and SEN are mainly constructed of alumina-graphite (AG) materials, and recently carbon-free (CF) materials are utilized for the inside liner. The CF inside liner has some superior characteristics for casting clean steels however one major challenge is thermal spalling due to high thermal expansion. The CF liner acts as a heat insulator reducing thermal shock due to its low thermal conductivity. Therefore when thermal expansion is reduced to a certain level, the CF liner is expected to improve thermal-spalling resistance of the LS and SEN. Through an investigation on various materials, we have developed the CF materials with relatively low thermal expansion. The effect of thermal expansion and conductivity on the thermal stress of the LS is evaluated by FEM. Conventional CF materials cause large thermal stress compared to LSs without CF liners. However, low thermal-expansion CF materials reduce thermal stress at the neck through a heat-insulation effect, reducing uneven temperature distribution.

1. Introduction

Ladle shrouds (LS) and submerged entry nozzles (SEN), used for the continuous casting of molten steel, are mainly made of alumina-graphite (AG) materials due to their high thermal-spalling resistance. Recently, "carbon-free" (CF) materials have also come to be used for the inside liner of the LS and SEN for the purpose of alumina-clogging prevention [1),2)], carbon pick-up prevention [3)], and corrosion prevention [4)]. Although CF materials have these superior properties, they are disadvantageous for preventing thermal spalling because of high thermal expansion. On the other hand, the CF liner acts as a heat insulation layer reducing thermal shock due to low thermal conductivity. Hence it may improve spalling resistance of the LS and SEN if thermal expansion is reduced to a certain level.

2. Experimental Procedure

2. 1 Preparation of materials

The CF materials were prepared by a standard method for producing LS or SEN. Several raw materials were mixed with phenol resin binder, and then formed in a rubber mold with CIP. The green body was cured at 200℃, and then heated at 1000℃ in a reducing atmosphere. The CF materials contain traces of residual carbon derived from phenol resin. However, the residual carbon easily disappears when the CF liner is exposed to molten steel; hence the CF materials are practically "carbon-free" during casting.

The chemical compositions and physical properties of the CF materials are summarized in Table 1. CF–1

Table 1 Properties of carbon-free materials

Material (CF)	1	2	3	4	5	6
Chemical composition /mass%						
SiO_2	—	33	3	56	33	22
Al_2O_3	73	50	97	41	60	45
MgO	27	—	—	—	—	—
ZrO_2	—	13	—	—	—	30
Apparent porosity/%	17.0	22.0	24.0	20.0	24.0	22.0
Bulk specific gravity	2.78	2.23	2.85	2.10	2.25	2.55

*1 President, Shinagawa Rongyuan Refractories Co., Ltd.
*2 Dr. Eng., Deputy General Manager, Shinagawa Rongyuan Refractories Co., Ltd.
*3 Dr. Sci., Manager, Shaped Refractories R&D Group, Research Center
*4 Shaped Refractories R&D Group, Research Center

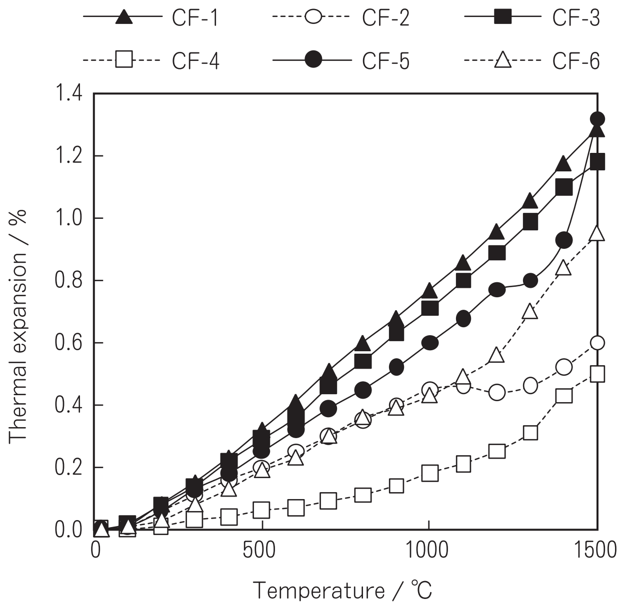


Fig. 1 Thermal expansion of CF materials.

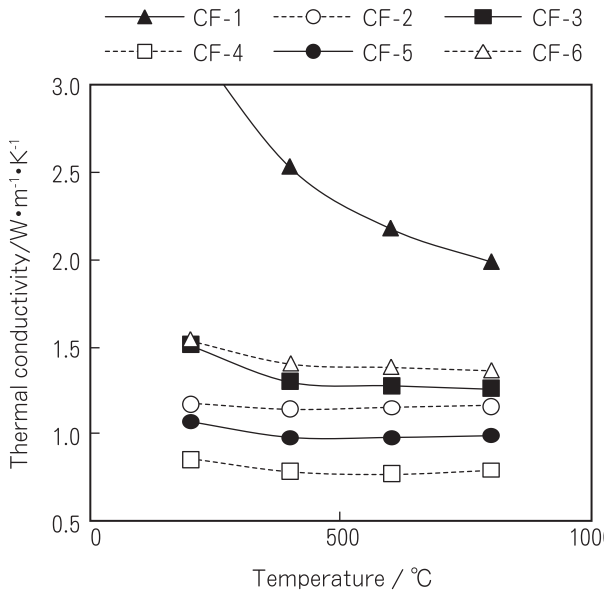


Fig. 2 Thermal conductivity of CF materials.

consists only of spinel, and is used for the SEN inside liner to reduce alumina clogging for Al-killed steels or to reduce inner-bore corrosion for high-oxygen steels[4]. Materials from CF-2 to CF-6 are Al_2O_3-SiO_2 materials with different SiO_2 contents. This type of CF material is effective in preventing SEN clogging in Al-killed steels, but in some cases the materials may be corroded by the [Mn] in molten steels[5]. Some materials were made using light-weight raw materials to reduce both bulk density and thermal conductivity.

2. 2 Experimental method

Thermal expansion was measured in nitrogen atmosphere by the non-contact laser sensor method (JIS R2207-1). Thermal conductivity is determined by the hot wire method (JIS R2251). Reactivity to [Mn] in molten steel is examined by dipping samples (size of 25×25×150mm) into molten high-manganese steel at 1560℃, 30 minutes, in an Ar atmosphere by using a high-frequency induction furnace.

3. Experimental Results

Fig. 1 shows the thermal expansion of the CF materials. The materials with more than 20 mass% SiO_2 tend to show low thermal expansion, but there are cases where a rapid increase in expansion is seen at high temperature (CF-5, 6). Standard AG materials used for the LS and SEN have 0.5-0.7% thermal expansion at 1500℃, most of the CF materials have higher thermal expansions than these AG materials.

Fig. 2 shows the thermal conductivity of the CF materials. All the CF materials have much lower thermal conductivity than the AG materials (12-25W/m·K). Spinel material (CF-1) has the highest thermal conductivity. The Al_2O_3-SiO_2 materials with lower bulk density (CF-2, 4, 5) have lower thermal conductivity.

In view of thermal spalling resistance, CF-4 seems to be the most suitable material for the inside liner because of the lowest thermal-expansion and the lowest thermal conductivity. CF-4 is, however, inferior in corrosion resistance against [Mn] in molten steel. Fig. 3 shows the appearance of CF-1 and CF-4 after being immersed into molten high-[Mn] steel. While the CF-1 retains its shape without corrosion, immersed portion of the CF-4 is corroded by [Mn] in molten steel. CF-4 is effective in preventing SEN clogging of Al-killed steels[4]. In the case of LS, the inside liner is required to be corrosion resistant to some extent for preventing local wear at a molten-steel impact area. Therefore we selected CF-2 as the standard inside liner material for the LS, particularly for LSs used in a non-preheating mode.

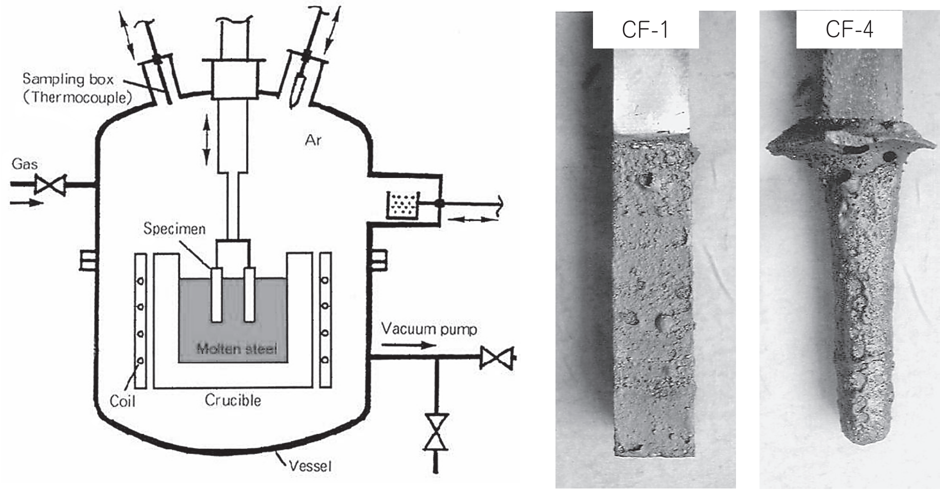


Fig. 3 Reaction test with molten high Mn steel.

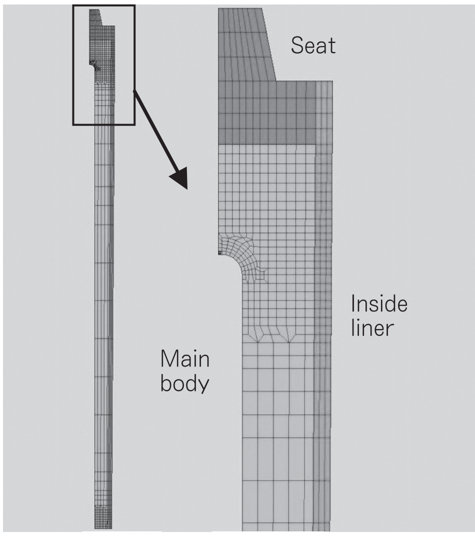


Fig. 4 Finite element modeling for ladle shroud.

Table 2 Properties of alumina-graphite (AG) materials

Material (AG)	1	2	3	4	5
Chemical composition /mass%					
SiO_2	5	20	25	23	—
Al_2O_3	85	55	50	47	66
C	10	15	25	30	30
Additives	—	10	—	—	4
Apparent porosity/%	19.0	12.5	15.0	14.5	16.0
Bulk specific gravity	2.82	2.55	2.35	2.31	2.58
Thermal expansion*1	1.14	0.57	0.55	0.62	0.89
Thermal conductivity*2	7.2	12.3	12.7	16.0	16.4

*1 : % at 1500℃, *2 : $W \cdot m^{-1} \cdot K^{-1}$ at 800℃

4. Finite Element Modeling

The effect of the thermal expansion and conductivity of the inside liner materials on LSs used in a non-preheating mode was evaluated by finite element modeling. Calculation model is shown in Fig. 4. The model consists of three parts; seat, inside liner (t=5mm), and main body. We calculated the thermal stress for various kinds of inside-liner materials. It was assumed that the entire inside of the LS is immediately subject to a molten steel temperature of 1570℃ without preheating, with an outer atmosphere equal to 300℃.

Table 2 shows the properties of the AG materials used in the calculation. The thermal conductivities of four kinds of the Al_2O_3–SiO_2–C materials increase with the increase in carbon content (AG–1, 2, 3, 4). Their thermal expansions are largely affected by not only carbon content but also SiO_2 content. AG–2 is a material which has high strength and high oxidation resistance. SiO_2–free Al_2O_3–C material (AG–5) has higher thermal conductivity and higher thermal expansion due to the lack of fused silica. As for other material properties required for the calculation, the modulus of elasticity was determined by 3-point bending test at 1000℃. The specific heat was estimated by chemical composition, and the Poisson ratio is assumed at a constant value.

Table 3 summarizes the material combinations for the calculation. Case 1 corresponds to the LS without a carbon-free inside liner. Cases 4–7 are not practical combinations, but they were calculated to examine the effect of thermal expansion and thermal conductivity.

Table 3 Material combinations for calculation

	Seat	Inside liner	Main body
Case 1	AG-2	AG-4	AG-4
Case 2	AG-2	CF-1	AG-4
Case 3	AG-2	CF-2	AG-4
Case 4	AG-2	AG-1	AG-4
Case 5	AG-2	AG-2	AG-4
Case 6	AG-2	AG-3	AG-4
Case 7	AG-2	AG-5	AG-4

Some examples of the calculation results are shown in Fig. 5. Large tensional stress occurs at outside of the seat, neck part, and lower end. These three stress areas correspond to changing shape or thickness. Among them, the actual thermal stress at the seat area is expected to be smaller than this calculation. This is because, in the case of actual casting, molten steel poured from the lower nozzle collides with the LS inner bore below the seat level. Empirically, typical cracking of the LS from thermal shock is horizontal cracking at the neck and vertical cracking at the lower end, both of which correspond to the calculated stress area.

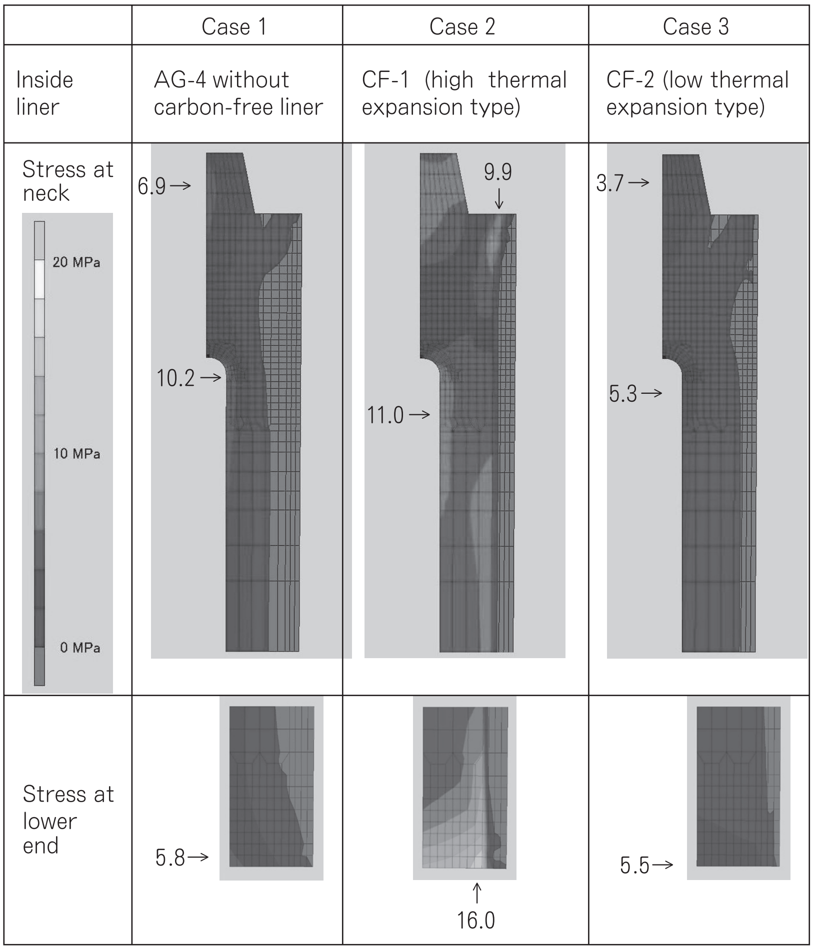


Fig. 5 Example of thermal stress calculation.

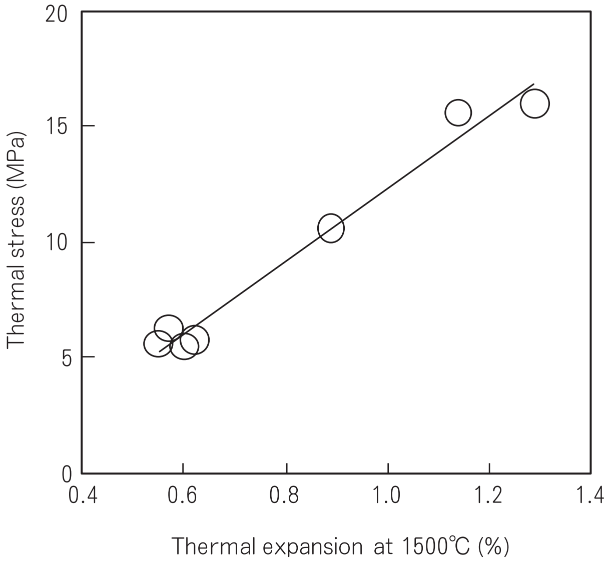


Fig. 6 Relationship between thermal expansion of inside liner and thermal stress at lower end.

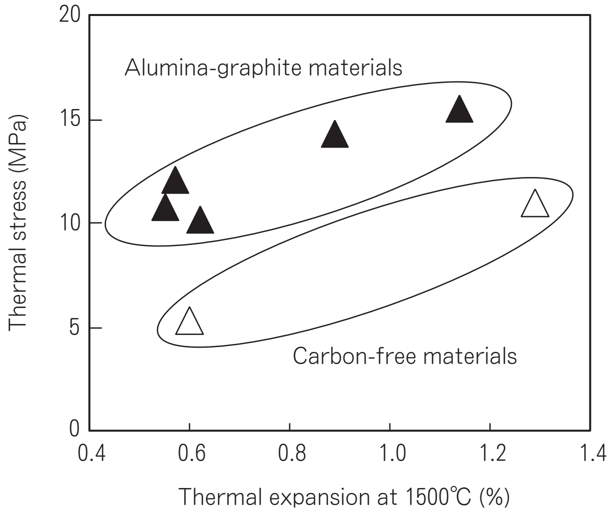


Fig. 7 Relationship between thermal expansion of inside liner and thermal stress occurring at neck.

Compared with Case 1 (without carbon-free liner), introduction of low thermal-expansion carbon-free CF-2 reduced thermal stress (Case 3). In particular, thermal stress at the neck was reduced to nearly half of Case 1. When high thermal expansion carbon-free material CF-1 is employed, large stress appears at the boundary between the inside liner and main body (Case 2).

Fig. 6 shows the relationship between thermal stress at the lower end and thermal expansion of the inside liner materials. The stress shows a good positive correlation with the thermal expansion regardless of the presence or absence of graphite (i.e. large difference in thermal conductivity) of the materials.

The thermal stress at the neck reveals a different trend between the carbon-free materials and AG materials (Fig. 7). Compared at the same thermal expansion, CF materials cause lower thermal stress than AG materials at the neck. This suggests that the low thermal conductivity of the CF inside liner contributes to reducing thermal shock at the neck area.

5. Discussion

When a cylindrical body like that of a LS is heated from the inside, tensional stress occurs on the outside due to thermal expansion on the inside. This stress peaks at the cylindrical end due to the deformation in the shape of a flared horn. Hence it is easy to understand that thermal stress at the lower end depends largely on the thermal expansion of the inside liner.

In the case of thermal stress at the neck, the reason why thermal stress increases there is probably due to the change in wall thickness, which causes uneven heat transfer. Fig. 8 shows the temperature distribution of a LS when the stress at the neck area increases. Compared with Case 1 (without CF inside liner), Case 3 (with CF-2 inside liner) shows steep thermal gradient within the inside liner and gradual thermal gradient within the main body. This suggests that the CF inside liner plays the role of a heat-insulation layer to reduce uneven temperature distribution around the neck just after the start of casting. Fig. 8 also suggests that the high temperature condition of the heat-insulating inside-liner could cause large thermal-expansion gap between the inside liner and the main body when the inside liner has high thermal expansion (Case 2). Therefore the CF inside liner should have low thermal expansion when the nozzle is used without preheating.

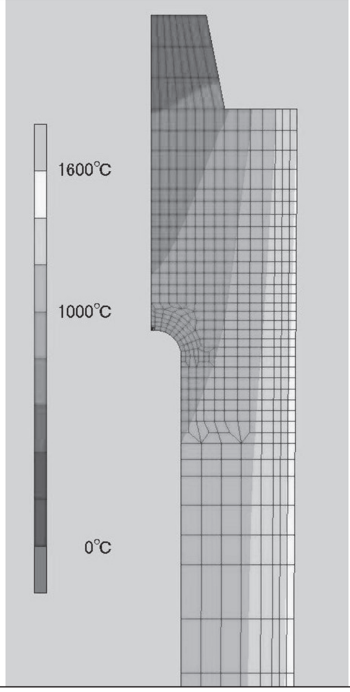
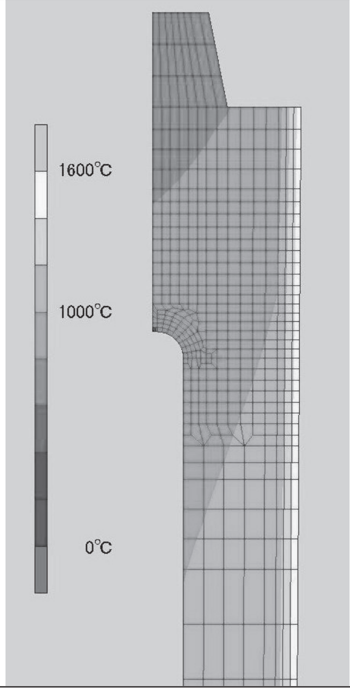
Case 1	Case 3
Without inside liner	With carbon-free No.2 inside liner
After 0.11 second from the start	After 0.26 second from the start
	

Fig. 8 Thermal distribution when thermal stress at the neck area reach maximum.

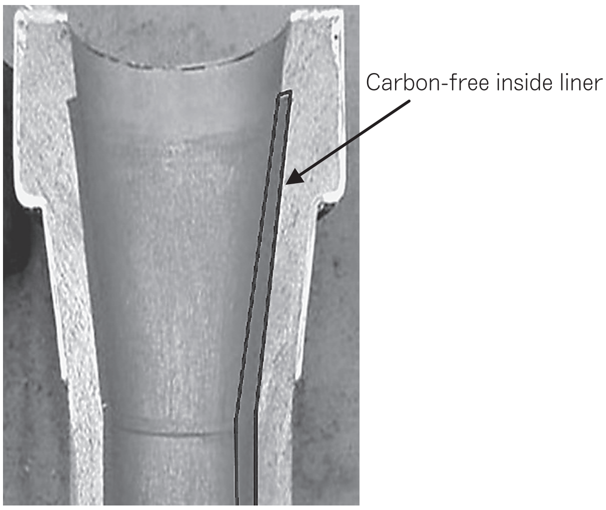


Fig. 9 Ladle shroud with carbon-free inside liner.

6. Spalling-resistant Ladle Shroud and SEN

LS and SEN with a heat-insulating and low thermal-expansion type of carbon-free inside liner have been put into practical use in Shinagawa Rongyuan Refractories (Fig. 9). These products are widely used by many customers, and their high spalling-resistance has been confirmed by practical results.

7. Summary

The carbon-free inside-liner performs as a heat insulation layer to reduce thermal shock due to its low thermal conductivity. Hence the low thermal expansion type of carbon-free materials effectively improves spalling resistance of the ladle shroud and SEN particularly at the neck area.

References

1) S. Tamura, T. Matsui, T. Ikemoto and K. Sawano : XXXIXth International Colloquium on Refractories, 118 (1996)
2) H. Kondo, N. Aramaki, O. Nomura, E. Iida, M. Takai and T. Horiuchi : Shinagawa Technical Report, **40**, 29 (1997).
3) Y. Wakao, M. Andou, S. Takahashi and Y. Okumura : XXXIXth International Colloquium on Refractories, 122 (1996)
4) O. Nomura, S. Uchida, W. Lin and T. Izaiku : Shinagawa Technical Report, **44**, 47 (2001).
5) R. Suzuki, W. Lin and M. Ogata: Taikabutsu, **62** [1] 20 (2010).