CHROME FREE MAGNESIA REFRACTORY DEVELOPMENT FOR RH DEGASSER APPLICATIONS

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ABSTRACT

The growing, and necessary, environmental effort made by industries to conserve the planet and its resources has been imperative, not only for the steel industry, but also for its suppliers, especially for refractory manufacturers, whose efforts are not only dedicated to environmentally correct products, but also products that enable customers to increase their productivity, reducing their carbon emissions.

Our research efforts have resulted in the development of new chromium-free magnesia products, dedicated to application in vacuum degassing furnace work linings, with corrosion resistance compatible with current chromium-containing products, which will be presented in this work. This is a long-researched but still incipient solution within refractory industry, however the application of which will be a major advance towards the definitive elimination of possible environmental contamination with hexavalent chromium.

1. INTRODUCTION

Emerged in the 1950s, vacuum decarburization technology in RH began to be disseminated at the end of the 1970s. Since then, it has undergone a constant evolution, becoming the main secondary refining route in integrated plants for the production of clean steel (1,2).

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Despite being used for many years in the refractory industry, chromium-containing raw materials had their application particularly expanded in the steel industry in the 1950s. The high corrosion resistance of the bricks, resulting from the "direct bonding" between chromium ores and magnesium aggregates, through which the grains are predominantly joined by a solid-state diffusion mechanism, represent a great performance advance for several applications (3), including the RH process. Since then, this type of material has been used successfully and its application has been unquestionable and difficult to replace.

However, the possibility of formation and release of hexavalent chromium to the environment, from chromium containing refractories (4), has represented a constant pressure for the development of refractory options without this element, and that can present a performance compatible with the current operational requirements. Some options have been developed and used for the application in question (5-8), however, none has reached a relevant and comprehensive performance as achieved by bricks containing raw materials with chromium.

Considering the immense environmental pressure, and the constant need for product evolution, the development of chromium-free products will be presented in this work, comparing them to conventional products containing chromium and with a notorious reputation in the world market of RH. The studies, which are still in their infancy, have shown that it is possible to achieve satisfactory, and even superior, corrosion resistance in environments with diverse and changeable slag, as is the case with RH operation.

2. MATERIALS AND TECHNIQUES

Free chrome bricks were formulated using high grade fused magnesia, high MgO content magnesia sinter and fused spinel of different grain sizes, necessary to provide an optimized grain sized distribution and densification. Ceramic additives were used in order increase corrosion resistance and modify thermal mechanical characteristics, especially thermal shock resistance. A chemical binder, activated at lower temperatures (< 500°C), was used to provide non-fired bricks, with lower CO2 emission impact. Table 1 provides a resume of investigated formulations. The physical chemical properties were determined after baking and after heat treatments at 1000 °C and 1450 °C, to evaluate their evolution during operation.

The developed materials were compared with current commercial direct-bonded MgO-Cr2O3 bricks used for RH lower vessel non-critical areas (Cr1) and lower vessel critical areas (Cr2), such as impact pads, throat and RH snorkels. Table 2 shows the chemical analysis and properties of chromium containing bricks.

Table 1 – Investigated non-fired MgO-Al2O3 formulations and their physical-chemistry properties.

Components (%)	A	D	G	H
Fused Magnesia (-5mm)	76,5	80,5	80,5	80,0
Magnesia Sinter (-1,0mm)	3,0	2,5	2,5	2,5
Fused Spinel (-1,0mm)	14,0	12,5	12,5	12,5
Ceramic Additive A	4,5	2,5	2,0	2,5
Ceramic Additive B	-	-	0,5	0,5
Chemical Binder	2,0	2,0	2,0	2,0
Properties (after baking)				
Bulk Density (g/cm3)	3,17	3,14	3,12	3,12
Apparent porosity (%)	9,1	8,9	8,8	9,6
Cold crushing strength (MPa)	74,1	74,8	84,8	77,4
Module of rupture (MPa)	11,6	14,4	18,3	16,8
After firing (1000 °C)				
Bulk Density (g/cm3)	3,12	3,10	3,07	3,08
Apparent porosity (%)	13,4	13,3	13,8	13,8
Cold crushing strength (MPa)	36,6	36,0	43,9	42,1
Module of rupture (MPa)	3,6	4,3	4,4	4,2
After firing (1450 °C)				
Bulk Density (g/cm3)	3,12	3,09	3,07	3,07
Apparent porosity (%)	13,4	13,6	13,9	14,0
Cold crushing strength (MPa)	39,9	37,9	37,1	40,3
Module of rupture (MPa)	4,1	3,5	5,0	5,2
Hot modulus of rupture (MPa) at 1400°C	1,77	1,40	2,15	1,85

Table 2 – Chemical analysis of MgO-Cr2O3 and their physical-chemistry properties.

Chemical Analysis (%)	Cr1	Cr2
MgO	67,0	67,2
SiO2	2,0	22,0
Fe2O3	7,0	5,6
Cr2O3	16,1	1,5
others	7,9	3,7
Properties (as received)		
Bulk Density (g/cm3)	3,08	3,21
Apparent porosity (%)	17,5	15,9
Cold crushing strength (MPa)	34,8	54,1
Module of rupture (MPa)	4,4	5,9
Hot modulus of rupture (MPa) at 1400°C	5,91	7,57

To evaluated the thermal shock resistance, the bricks were submitted to a several thermal shock cycles at 1000 °C (1 hr minutes) and air (forced convection) until room temperature, and them their sonic elastic modulus was determined after cycles 1, 2, 4, 6, 8 and 10. The developed bricks were previously heat treated at 1450 °C per 5 hours, before to be submitted to thermal shock test. All the materials were compared considering the residual percentage of the original Young Modulus.

Corrosion resistance was determined using a rotate slag test furnace, at 1680 °C (+/- 20 °C), using a FeO rich slag (F2) and a CaO/Al2O3 slag. The slag chemistry analysis is presented in Table 3. For each test, the slag was renewed in the middle of the test, resulting in a two corrosion stages with new slag. The slag/refractory interface was simulated applying the software FactSage 8.0, using the databases FactPs, FToxid and FTmisc. The software was used to simulate the equilibrium condition of a hypothetical interface varying from 100% of slag to a 100% of refractory, showing what are the phases which could be expected for at a simulated condition considering an operation at 1700°C and 0,004 atm (approximately vacuum condition inside the RH). The FactSage simulation were done for both slags considering one MgO-Cr2O3 brick (Cr2) and one MgO-Al2O3 brick (G).

Table 3 – Chemical analysis of FeO rich slag (F2) and CaO/Al2O3 slag (C2).

Chemical Analysis (%)	F2	C2
Fe2O3	39,3	-
CaO	34,2	40,4
Al2O3	16,8	55,8
SiO2	6,5	-
MgO	3,2	3,8

3. RESULTS AND DISCUSSIONS

As previously presented, Tables 1 and 2 showed that the developed formulations have a lower porosity than commercial MgO-Cr2O3 products. This can be an interesting feature to be considered in relation to the penetration of slag during the use of the products.

The different heat treatments applied to the developed products showed a good evolution of cold mechanical resistance, with the values after heat treatment at 1450 °C at the same level as those observed for the MgO-Cr2O3 products. However, the developed products presented values of hot mechanical resistance of the order of a quarter to a third of the values presented by the commercial products containing chromium. In isolation, these lower values may not say much, but they can be very important if considered together with the resistance to thermal shock and to the appearance of cracks by thermomechanical stress, very common in more critical regions of the RH furnace, such as the throat and snorkels, especially in those cracks that occur at the interface between volumes impregnated with slag and volumes still unaltered, which greatly contribute to the structural spalling of the bricks in operation.

As seen in Figure 1, the thermal shock resistance test showed that the commercial product containing chromium used in the critical parts of the RH furnace, Cr2, presents the best evolution of the residual elasticity modulus. However, the commercial chromium containing product used in the less noble regions, Cr1, showed a lower retention of the elastic modulus over the thermal shock cycles. The developed products A and D showed a very similar behavior to the chromium containing product, Cr1, while the products G and H presented better behavior for the retention of the elastic modulus, and the product G was very close to the product Cr2. This shows the effectiveness of the ceramic additive A in improving the thermal shock characteristics of the developed material.

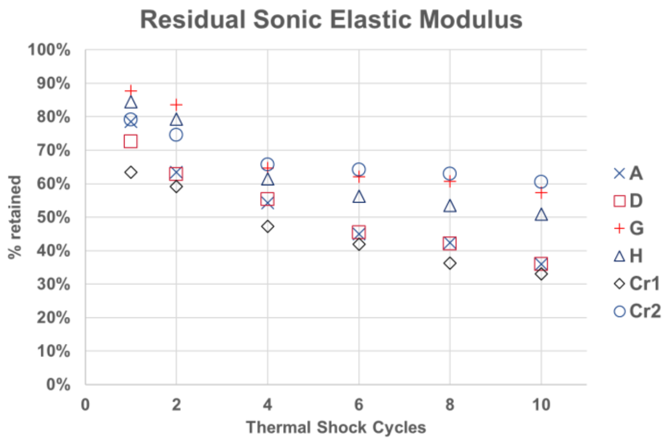

Figure 1 – Residual sonic elastic modulus for developed products (A, D, G and H) and commercial chromium containing products (Cr1 and Cr2).

The RH furnace slag changes throughout the operating cycle, starting from a normal steel ladle slag, evolving into a FeO-rich slag, and ending up in a CaO/Al2O3 system slag (9). Based on this observation, tests were carried out on a slag rich in FeO (F2) and a slag from the CaO/Al2O3 (C2) system, as suggested in other studies. The results for these tests are shown in Figure 2 to Figure 5.

In case of FeO rich slag F2, the formulations developed proved to be more resistant in the corrosion test, both in the corrosion itself and in the impregnation aspect, as shown in Figures 2 and 3. Comparing product to product, formulation H had the best performance in the test with slag rich in FeO.

Considering the slag of the CaO/Al2O3 system, characteristic of the end of the processing in the RH furnace, the formulations G and H, conceived with the ceramic additive B, showed a better performance.

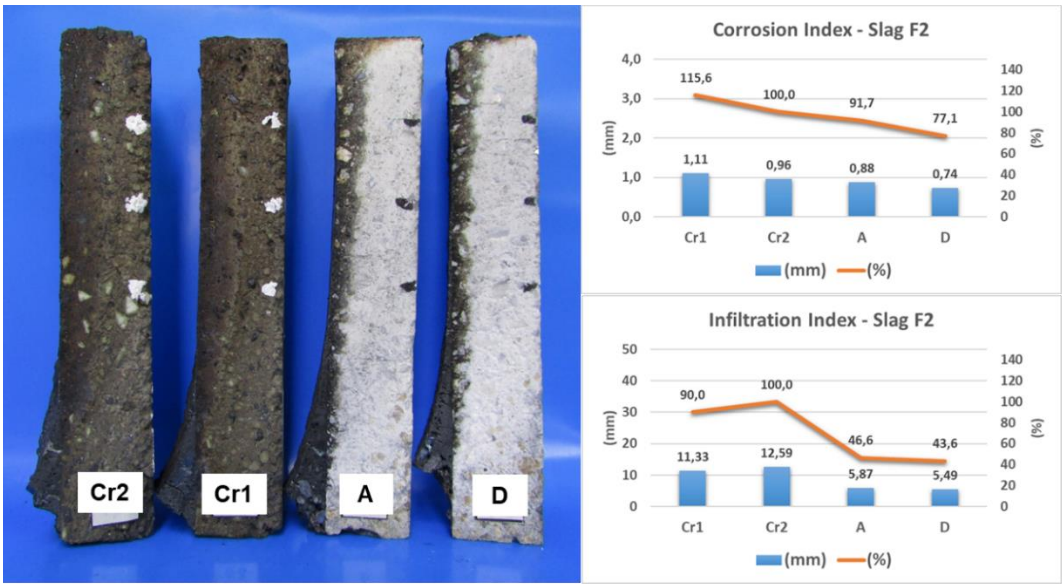

Figure 2 – Results for chromium containing commercial bricks and formulations A and B submitted to a corrosion by FeO rich slag F2.

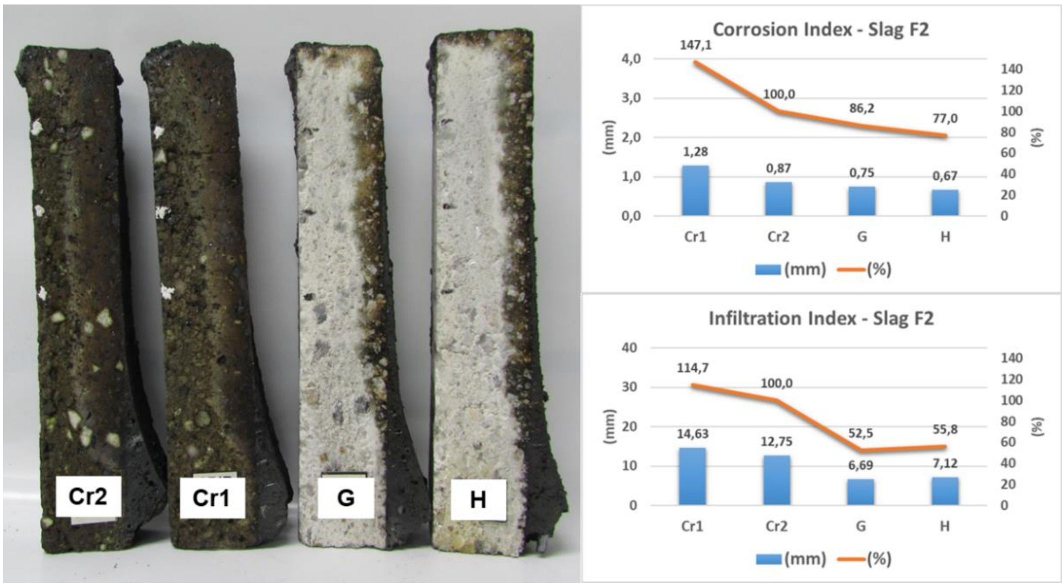

Figure 3 – Results for chromium containing commercial bricks and formulations G and H submitted to a corrosion by FeO rich slag F2.

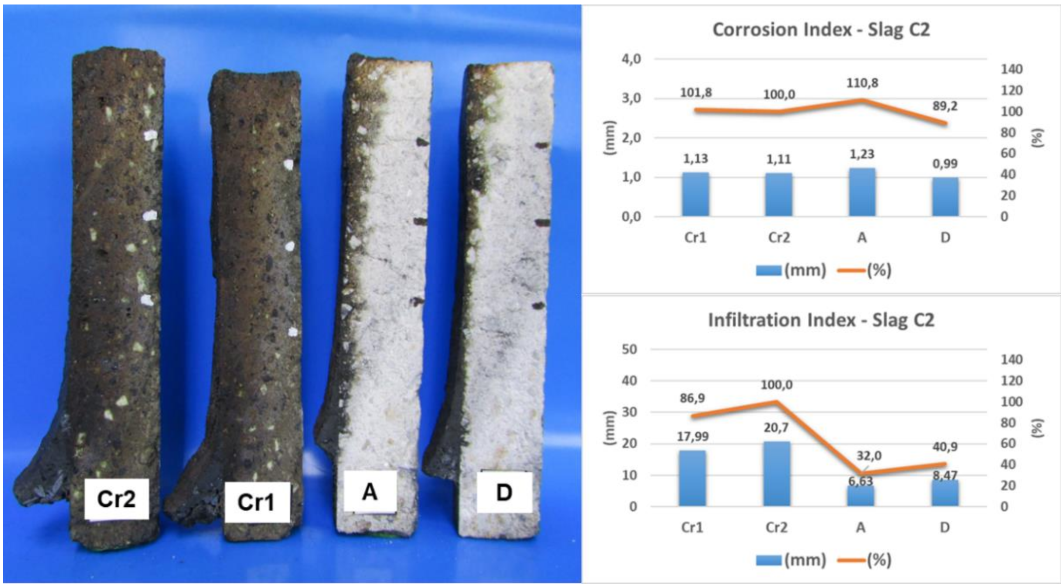

Figure 4 – Results for chromium containing commercial bricks and formulations A and B submitted to a corrosion by CaO/Al2O3 slag C2.

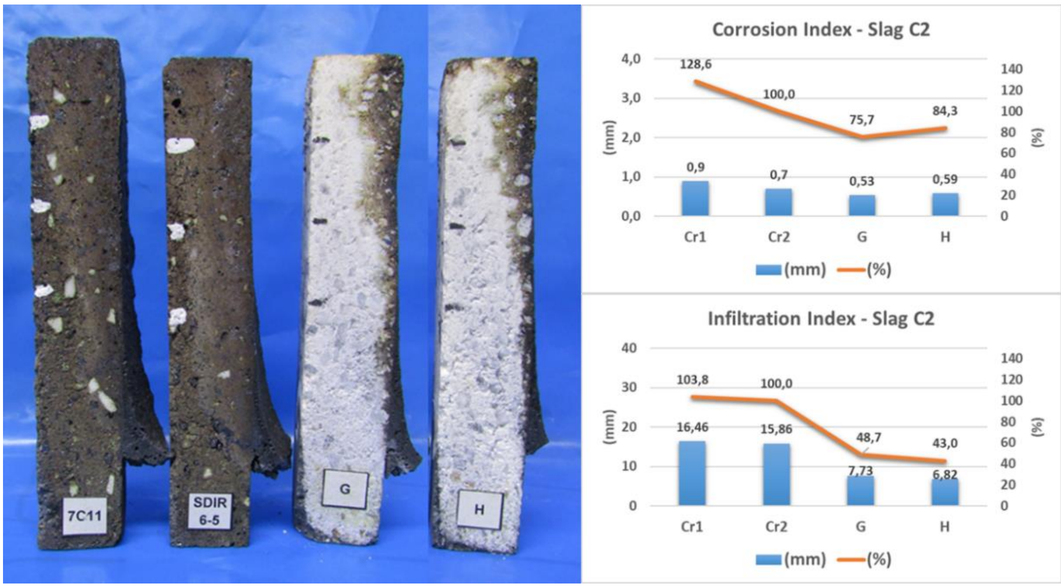

Figure 5 – Results for chromium containing commercial bricks and formulations G and H submitted to a corrosion by CaO/Al2O3 slag C2.

When considering the performance of the thermal shock resistance tests and the good results of the corrosion tests, the formulation G was chosen, together with the commercial product Cr2, for a simulation of phases in equilibrium at the slag/refractory interface, at temperature and pressure similar to the operating conditions, using Factsage 8.0 thermodynamic simulation software. The results are shown in Figures 6 and 7, respectively for slag F2 and C2.

In the case of the simulation with the FeO-rich slag, shown in Figure 6, the interface of the commercial product containing chromium shows an initial solubilization of the refractory of about 17%. after this point, MgO saturation occurs, which becomes stable. The saturation of chromium spinel, on the other hand, saturation occurs later, in a fraction around 20% of refractory. During all simulated fractions, there is a small evolution of the gas phase, rich in O2. There is no precipitation, in equilibrium, of phases other than those initially present in the refractory.

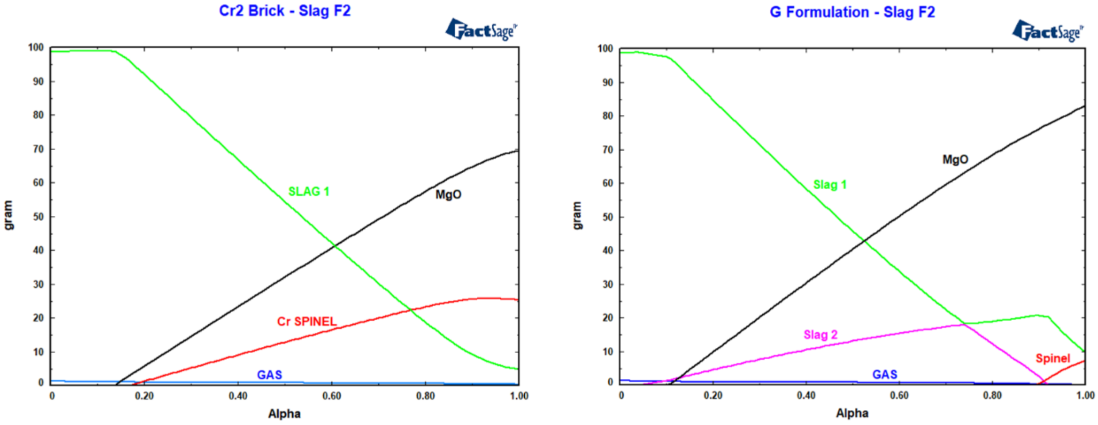

Figure 6 – Equilibrium phases, at 1700°C and 0,04 atm, predicted by FactSage 8.0, considering the chromium containing brick Cr2 and formulation G, into the hypothetical slag F2/brick interface, varying from 100% slag (Alfha = 0) to 100% refractory (Alpha = 1).

In the case of formulation G, the initial solubilization of the refractory, at the interface with the FeO-rich slag, is close to 15%. The additive ceramic phases A and B are completely solubilized, and the system, in equilibrium, presents, for proportions above 15% of refractory, two immiscible slags. The spinel phase only becomes stable in a proportion of above 90% refractory. There is also the presence of a gas phase rich in O2 in practically all refractory proportions.

In the case of the interface with the C2 slag (CaO/Al2O3), the commercial refractory containing chromium has a lower solubility than in the F2 slag, with chromium spinel already saturating the slag from about 7% of refractory fraction. No gas phase is present.

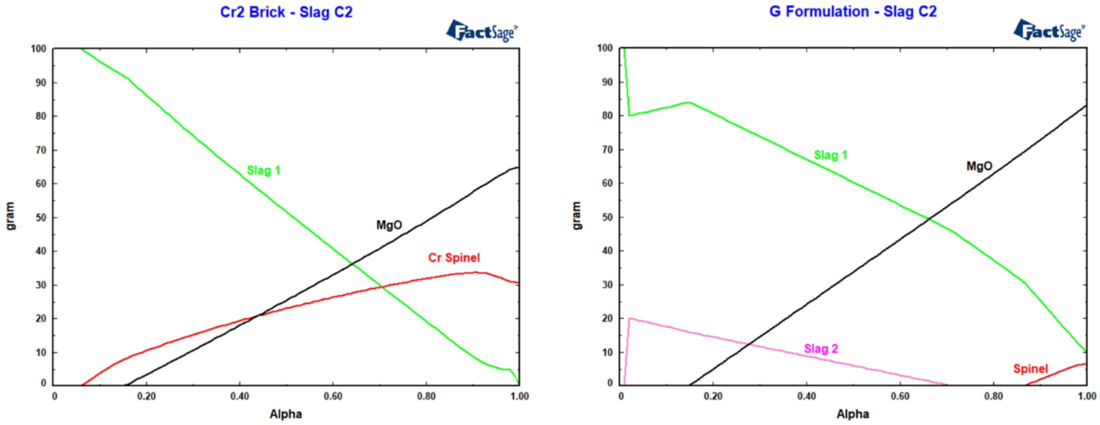

Figure 7 – Equilibrium phases, at 1700°C and 0,04 atm, predicted by FactSage 8.0, considering the chromium containing brick Cr2 and formulation G, into the hypothetical slag C2/brick interface, varying from 100% slag (Alfha = 0) to 100% refractory (Alpha = 1).

In the case of the refractory/slag interface for formulation G, the initial solubilization is much higher than for the product containing chromium, around 18%. Again, the additive ceramic phases A and B are not stable at all refractory ratios, and two immiscible slags are present up to the 70% refractory ratio. No gas phase is present at equilibrium conditions, and the spinel phase only becomes stable from a proportion of about 88% refractory.

From the data observed in the corrosion tests and in the phase equilibrium simulations, it is possible to assume that the presence of two immiscible slag phases, present in the MgO-Al2O3 system, combined with the complete solubilization of the additive ceramic phases A and B in these same slags, play a key role in the improved corrosion and penetration resistance presented. However, further investigations are underway, considering the concentration of these phases in the matrix of these new materials, and their interaction with the evaluated slag.

4. CONCLUSION

The present work showed the successful development of MgO-Al2O3 system formulations compatible with some of the main characteristics presented by chromium-containing products used for applications in RH vacuum degassing furnaces. Those products were developed using a lower heat treatment temperature, reducing CO2 emissions in comparison to traditional chromium containing materials.

A superior corrosion resistance was achieved by the materials developed, mainly by the aid of ceramic additives that, through their solubilization, provided a smaller extension in the impregnation by the evaluated slags.

Satisfactory levels of resistance to thermal shock were achieved, compatible with a commercial reference product containing chromium, used in critical regions of the RH furnace, such as throat and snorkel.

Future studies will focus on improving the hot mechanical resistance, necessary to prevent the appearance of cracks in current commercial products, due to the very characteristic thermomechanical effects present during the operation of RH furnaces.

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