M.H. Amin , A.A. Salardini, Mohsen Amin-Ebrahimabadi

Corrosion and deterioration behavior of thermite welding alumina crucible used in railway

Mohamad Hassan Amin

He got Ph.D. Degree in Material Engineering (Ceramics) from the Material and Energy Research Centre (Ministry of Science, Research and Technology, Tehran) in 1999. He was employed by the Shimipejouheshyar Company as a director of production for magnesia and alumina refractories products from 1989 to1992. He also worked as vice chancellor (head of research) in Azad University of Yazd for 2 years. He then joined the faculty of Materials and Energy Research Center (MERC) in 1999 . He is now in the MERC as an assistant professor in the Ceramic Department.

Thermite welding of rails is now a standard operating practice to successfully join rails conjunctions in the field. Alumina crucible, an essential component of this operation, will be damaged and unusable after not more than 30 operations. This is due to direct contact of crucible with molten iron. Factors influencing this damage, including chemical reactions, penetration and infiltration of molten iron into the body, were studied using a scanning electron microscope equipped with X-ray spectroscopy (SEM/EDS) and X-ray diffraction. The results of this study supported by the kinetics of reaction between iron melt and alumina crucible in thermite welding showed that the thermite process does not significantly affect the crucible body component chemically; i.e. corrosion was not a major factor in crucible deterioration. The penetration and infiltration of melts into the crucible body via the grain boundaries and porosities were the major factor. A higher rate of the melt penetration into the parts containing impurities especially the silica was more harmful.

1. Introduction

The Fe_2O_3/Al mixture is a classical thermite system which has been used since 1898 on the welding of railway tracks[1]. Thermite welding of rails is now a standard operating practice to successfully join rails conjunctions in the field. The chemical reactions associated with the thermite process are highly exothermic and therefore release tremendous amounts of heat, which can be used for welding. The heat of reaction of the thermite system described by Eq. (1) is sufficient to raise its temperature to very high values (about 2700 °C), above the melting points or even the boiling points of reactants, intermediate and final products[1]:

$$Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3 + \sim 850 \text{ kJ} \quad (1)$$

Materials and Energy Research Center, Meshkindasht Road, Poste code: 3177983634, Karaj, Iran

The reactions used for welding processes are between fine aluminum and iron oxide powders which are ignited in a crucible. This operation is new to the Iranian railway industry. The crucible is an essential component in which the initial chemical reaction, melting of the charge and slag separation takes place. As such it must be able to withstand very high temperatures over a number of welds. Although single-use crucibles have recently been used in many countries, due to technology and cost limitations, multiple-use crucible is the only choice the railroad industry in Iran have.
The number of uses of crucibles in this industry is comparatively lower than reported elsewhere[2]. One of the reasons may be the quality of crucible body and its low resistance to corrosion or breakage. Corrosion produces a deterioration of the crucible resulting in melting or breakage.
Very little information is available in relation to extension of life of multiple-use crucibles and its relation to the rate of corrodibility or defects of the body. In this work we use the corrosion term as the chemical reaction between the body and the melted materials inside the crucible which could be expedited by melt infiltration into crucible body.
The objective of this research was studying the corrosion process in order to recognize the process of crucible deterioration, so that in the future the production conditions and ways of preventing damages can be optimized.

2. Experimental

Post-mortem assessment of spoiling problems was done in a refractory crucible when thermite reaction occurred. An alumina insulator crucible was used as container of the reactant powder mixture. A schematic figure of the crucible is shown in Fig. 1. The commercial thermite powder provided by the Iranian railway company was used. The crucible was placed in a case to be warmed up to 100 °C. The bottom part of crucible was closed with an automatic thimble type ATS-ER and the surface was covered with refractory magnesia powder. The crucible was filled with 9 kg of thermite ignition powder and the required energy was supplied by torpedo.
The melt/slag penetration was determined on a cut face of the crucible mounted in epoxy resin. Chemical analyses were performed using X-ray fluorescence spectrometry (ARL XRF). X-ray diffraction was used to identify phase changes using a Philips-112 X-ray diffractometer, in the angle range 5 to 80° with a step size of 0.02°. The cross-section of the used crucible was examined by optical microscopy (Zeiss Oxio-Vert 200) and the observation of microstructure was performed on polished faces using a scanning electron microscope (SEM) equipped with X-ray spectroscopy (LEO 460). The apparent porosity and density were determined according to ASTM C20-87. The pore size distribution was determined by a mercury porosimeter according to DIN EN 993.

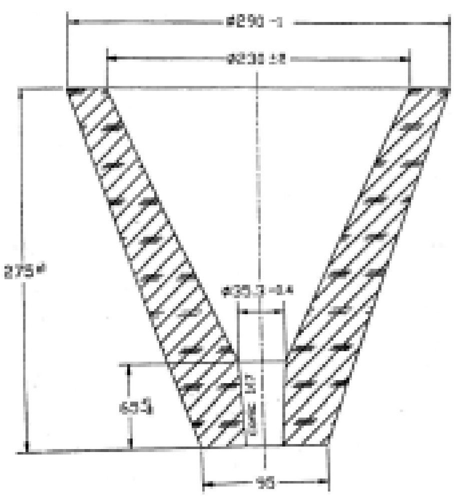

Figure 1. Schematic figure of crucible

3. Results and discussion

The wet chemical analysis of the unused crucible body is presented in Table 1. The main components are Aluminum oxide with small impurities.
Due to the addition of impurity (iron powder) to the thermite powder, the temperature resulting from this reaction is approximately 2090° C[2]. Due to this high temperature the body of the crucible becomes corroded and after 30 cycles, it became unusable. The section of crucible most corroded was the funnel-shaped area, where the diameter of the crucible reduced and the crucible was just in contact to melt, in another words, the slag does not have any significant role in the corrosion process.

Table 1. Chemical components of tested refractory crucible

Oxide	Al_2O_3	SiO_2	Fe_2O_3	Na_2O
wt %	96,34	1,99	0,68	0,99

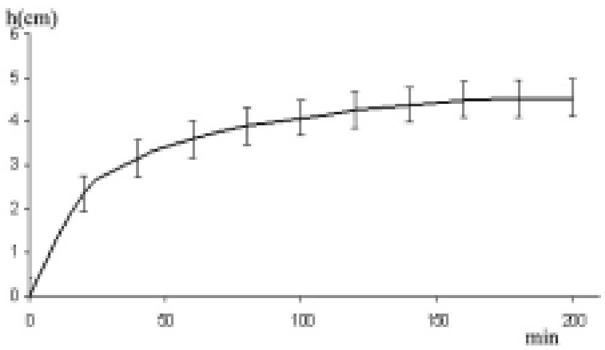

Figure 2. Relation between thermite reaction time (min) and thickness of corroded crucible (cm)
(Bars refer to standard error)

As shown in Fig. 2, the relationships between the thermite process, time and thickness of corroded crucible is parabolic, an indication the corrosion rate to be controlled by a diffusion mechanism[2,3].

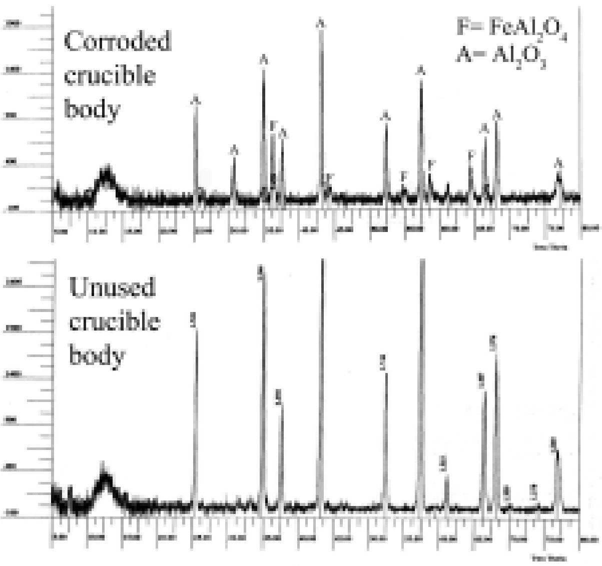

Figure 3. XRD pattern of the corroded crucible body vs. the unused crucible body

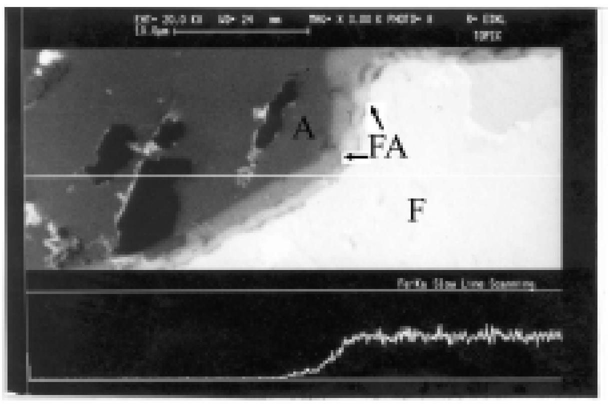

Figure 4. SEM micrograph of the surface of corroded parts with Fe line scan

In this case, the corrosion rate is controlled by indirect mechanism as a result of formation of a dense solid spinel layer at the melt/refractory interface. According to references and phase diagrams, formation of the $FeAl_2O_4$ (FA) spinel layer would be expected[4]. Reaction and dissolution of Al_2O_3 in molten iron (or slag) can be directly or indirectly dependent on whether an FA spinel layer forms at the melt/crucible interface. As it is evident from the X-ray diffraction pattern in Fig. 3, the FA spinel was produced by the reaction between the melt and alumina crucible. When comparing the XRD pattern of the corroded crucible body with that of the unused crucible body, some new peaks in the XRD pattern of the corroded crucible body could be seen. In this pattern in addition to significant Al_2O_3 peaks, other peaks of d 2.475, 2.905, 1.446, 1.576, 2.046 and 1.677 Å were also observed that match with PDF34-192 related to $FeAl_2O_4$ spinel component.

It was confirmed that there was a dense layer between the refractory and the melt after the thermite reaction. Fig. 4 shows a backscattered electron image of the interface area between the refractory (A) and melt (F) and the dense layer (FA). The typical elemental analysis patterns of these phases are shown in Fig. 5.

The dense layer of spinel prevented the coating material from being penetrated by melt / slag during service. Since the T_m of FA spinel is 2135 °C, well above the casting temperature (about 2093 °C), and it is stable in high alumina slag, its formation reduces corrosive wear[5]. The value of activation energy for the diffusion of Fe in the FA phase is high (273kJ/mol)[6]. It can be therefore be inferred that the diffusion of Fe into $FeAl_2O_4$ controls the product of reaction. Based on the prediction results of kinetics equation for corrosion, the destruction should happen after 200-thermitee cycle[2], while in practice it will occur after only 30 to 40 cycles.

By increasing the number of thermite reaction cycles, molten Fe infiltrated via the porosities in different parts of the crucible. One of the important points is that the melt that entered in some parts of the crucible could results in visual destruction, but in most infiltrated parts, we cannot find a significant sign of destruction. Closer visual studies show that the crucible destruction will happen just in parts where the molten iron touches

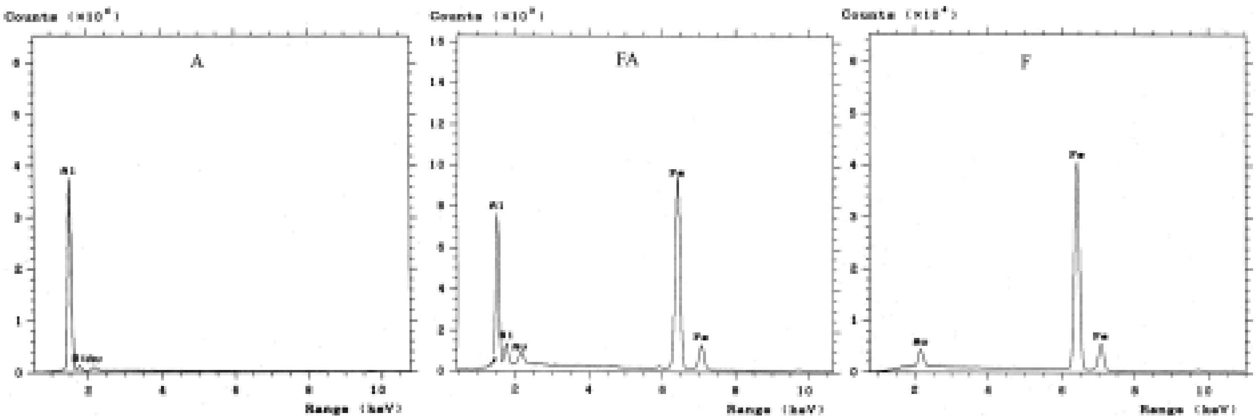

Figure 5. Typical elemental analysis pattern of the phases as shown in Fig. 4

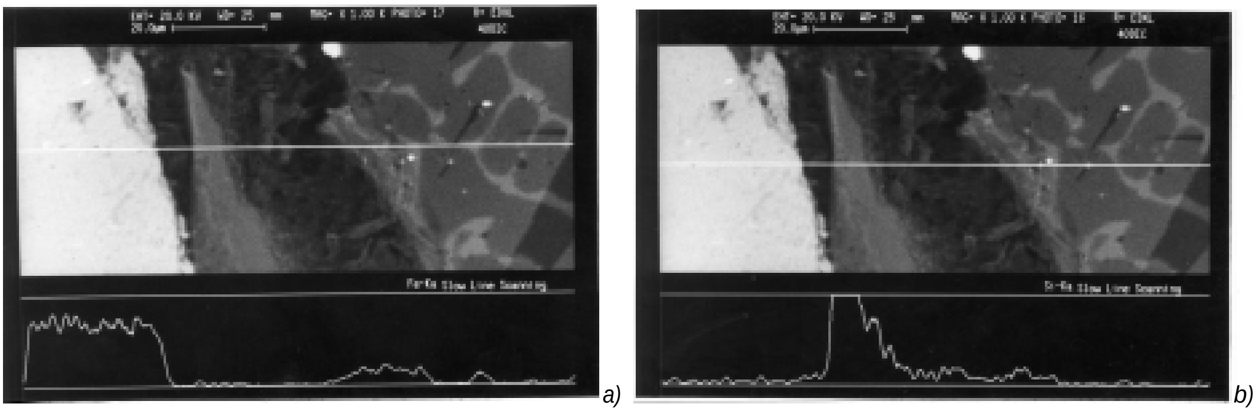

Figure 6. SEM picture from the surface of a ruined part in the body: a) Fe line scan and b) Si line scan

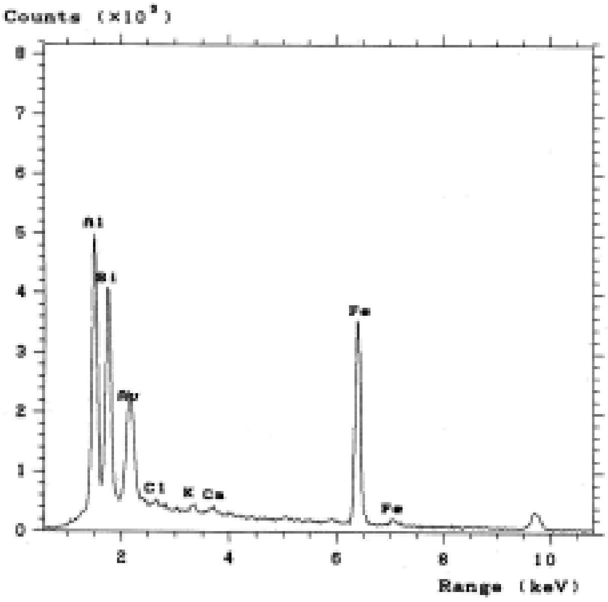

Figure 7. X-ray spectroscopy of damaged part of the crucible

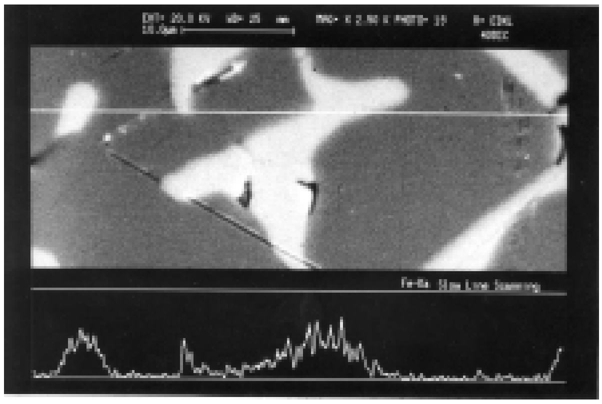

Figure 8. SEM micrograph of the corroded parts with Fe line scan

the existing impurities specially silica in the body. In Fig. 6 a destroyed part of the body with line scan elements of Fe and Si are shown.
Under these conditions, no reaction occurs between iron and SiO_2 and they will be separated in solid conditions[4]. XRF of clear phase in the damaged parts shows that the elements of Al, Fe and Si were present. Figure 7 presents the X- ray spectroscopy of this phase in the damaged part of the crucible.
Examination of the corroded samples revealed that the melt penetrates inside the body only via the grain boundaries and porosities. This point may be seen in Figure 8 in which the corroded part of the crucible is shown after performing 6 thermite cycles with Fe line scan. The figure also shows that the molten iron is distributed at the grain boundary of the refractory body. When the melt is formed at the surface of the refractory crucible, the free oxygen will move towards the bulk in the refractory and produce FeO. Considering the high molar surface tension and its reversal relation with viscosity, it may be expected the formed melt to have a low viscosity; therefore, the melt could easily enter the crucible body. Melt distribution more abundant in the grain boundary and crucible cords confirms this low viscosity.
The presence of heterogeneity in the basic components of the body, leads to the collection of impurity oxides in specific areas of the body; therefore, when the melts penetrates in those parts, the corrosion will increase at higher rates and causes destruction.

4. Conclusions

The thermite process was shown not to chemically affect the crucible body component significantly. In another word corrosion of crucible is not a major factor in its deterioration. The main reason for deterioration of the body and reduction of crucible life is the penetration and infiltration of melts into the crucible body via grain boundaries and porosities.
In addition, penetration of melt into the body does not solely lead to destruction. In fact the real factor is the high rate of the melt penetration into the parts where molten iron touches the existing impurities specially the silica in the body.

References

1. Luisa Duraes, Benilde F.O. Costa, Regina Santos, Antonio Correia, Jose Campos, Ant´onio Portugal, "Fe_2O_3/aluminum thermite reaction intermediate and final products characterization", Materials Science and Engineering A 465 (2007) 199-210.
2. Mohamad Hassan Amin, R. Emami, A. Kazemzadeh, M. Solati, "Evaluation of the Mechanism And Kinetics of Reaction of Iron melt With Alumina Crucible used Thermit Welding Railway", Proc. of 2nd International Conference on Chemistry and its Applications (University of Qatar), 2003, 656.
3. Mohamad Hassan Amin, A. Kazemzadeh, M. Amin-Ibrahimabadi, N. Saha-Chaudhury and V. Sahajwalla, Investigations of Calcium Aluminate Slag Penetration to MgO Monolithic Refractories in Steelmaking Process", J. Industrial Ceramics, Vol. 2(2008) 125-132.
4. E.M. Levin, C.R. Robbins and H.F. Mc Murdie," Phase diagrams For Ceramists", The American Ceramic Society Inc., 1964.
5. Winchell, " Elements of optical mineralogy", National Bureau Standard (VS) Monograph, 25, 19, 1982, 48.
6. Run-Hua Fan, Hong-Liang L¨u, Kang-Ning Sun, Wan-Xia Wang, Xin-Bing Yi, "Kinetics of thermite reaction in Al-Fe_2O_3 system", Thermochimica Acta 440 (2006) 129-131.