SPINELS AND REFRACTORIES

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Although alumina-magnesia spinel containing brick and monolithics are currently in wide use, they are by no means the first nor the only spinel bearing refractories available. Over time, chrome, magnesia-chrome, alumina-chrome and now alumina-magnesia spinels have all been used to impart important high temperature properties to refractories.

SPINEL, DEFINITION

There is some confusion as to what constitutes a spinel. The source of the problem is that spinel, the mineral ($MgAl_2O_4$), is part of the spinel group, general formula $R_8^{+2}R_{16}^{+3}O_{32}$, and there is seldom a distinction made between these two entities. The spinel group consists of many minerals amongst them: spinel, chromite, magnetite, etc. Deer, Howie and Zussman [1] list 13 end members, which can be sub-divided into three series depending if the trivalent ion is Al, Fe or Cr. Pure end member minerals are rare in nature and, they exhibit extensive solid solution between Mg, Fe, Cr, Al, Zn and other cations.

Even though I just clarified the term spinel, I will use it the way it is common practice in the refractory world; i.e. without distinguishing between the mineral and the group.

CHROME

The first documented experimentation of chrome as a refractory material was in 1879 in the open-hearth furnaces at Terre Noire, France [2]. In the 1880s, chrome refractories were already in use in large scale in the Petersburg- Alexandrofsky steelworks [3]. By 1886 several European open hearths had installed them and, around 1896 they could be found in use in the USA [2].

The early chrome refractories consisted of molded and fired chrome ore which is a mixture of different minerals, in particular of spinels. Its predominant phase is chromite (Cr_2O_3), but it also contains alumina (Al_2O_3), magnesia (MgO), silica (SiO_2), iron oxide (Fe_xO_{x+1}), etc. Chromite is a so-called mixed spinel of the type $R^{+2}OR^{+3}O_3$ [3]. It readily reacts with iron oxides forming a solid solution, which, in service, leads to an increase in porosity and the subsequent expansion of the brick, the phenomenon called bursting. Additional challenges when using these brick consisted of crumbling because of exposure to alternating oxidizing and reducing atmospheres while at temperature and, continuous shrinking and softening as a function of high temperatures, which limited their applicability. To address these problems, magnesia was added to improve their refractoriness and to create a composition with better slag and thermal shock resistance. Poirier and Bouchetou's [4] contrasted the ternary MgO-FeO-Fe_2O_3 phase diagram with a slice through the 40% Cr_2O_3 level quaternary showing how the presence of chrome oxide extends the spinel region of the MgO-FeO-Fe_2O_3 field thereby improving the refractory's corrosion resistance in the presence of iron oxide.

MAGNESIA CHROME

Magnesia chrome, also called periclase-chrome, refractories date from the early 1930s when they were simultaneously developed in several countries [2, 3]. By about 1935, chemically bonded and fired brick had become available. In the late 1950s and 1960s work on firing temperatures and their effect on the brick microstructure elucidated the mechanism behind direct bonding (DB) which was defined as "….direct periclase-spinel and periclase-periclase bonds" [3]. By developing a ceramic bond between these high melting point minerals, improved slag resistance and high hot strengths could be achieved. In 1952, the first fusion cast magnesia chrome blocks became a reality. The use of fused grain obtained through this process greatly improved the high temperature properties of the refractories made with it and it is still one of their major components.

When I started working for the steel industry, magnesia chrome refractories were the go to type of refractory for demanding environments. They could be found in all areas, from open-hearth furnaces, which had a never-ending appetite for all sorts of brick, to reheat furnace hearths to many other applications in between. They were also used extensively in other industries. Today, many of these processes are no longer and magnesia chrome refractories are found only in select applications: alloy and specialty steels converters, steel degassers, melting/refining vessels for copper and lead, some coal gasifiers and cyclones and, a few others.

The 1970s and early 1980s were an exciting time in that much work was carried out in furthering the understanding and technology of magnesia chrome refractories: their wear, the required bond properties for best life in different slag environments, the slag chemistries needed for refractory compatibility, etc. This enthusiasm was dampened considerably in the USA when, in 1986, the Environmental Protection Agency (EPA) released its maximum leachable chromium level mandate as the result of attempting to regulate the pollution created by the chromium used in industries such as chrome plating, leather tanning, and textile manufacturing. Refractories were not part of the original "offending" industries, but found themselves drawn in because of magnesia-chrome refractories and the danger of formation of Chrome (VI) at high temperature and in the presence of alkalies, in particular, lime. The problem is that Chrome (VI) is highly soluble in water and could find its way into the water systems if the used linings were simply dumped. Today, most countries have some type of regulation [5, 6] addressing the disposal of chrome bearing refractories resulting "…from the recognition of hexavalent chromium as a known human carcinogen …" [7]. Lee and Nassaralla, published several studies [8, 9] based on work carried out on used magnesia chrome refractories recovered from industrial processes. The used brick had been exposed to known temperatures and slag environments and were compared to as received samples to determine the fundamentals of Chrome (VI) formation. Because of this and the work of many others in academia and in the refractory's industry, the use and disposal of chrome bearing refractories, no longer present a problem.

ALUMINA CHROME

Other chrome bearing refractories have been manufactured, but only alumina chrome is routinely used. In the late 1970s alumina chrome brick were developed [10] containing chromic oxide instead of chrome ore. This functions as a sintering aid allowing for the direct bonding at firing temperature without resorting to silica and leading to a highly refractory product which also has very good slag and thermal shock resistance. The refractory color change from green to a deep red signals the completion of the spinel forming reaction. If the spinel so formed would be of gem quality, it would be called a ruby. Prior to firing, these refractories present the same disposal challenges as the magnesia containing ones.

ALUMINA MAGNESIA

The impetus for the development of the Al_2O_3-MgO spinel refractories was as a replacement for the magnesia-chrome due to their possible disposal issues. Al_2O_3 -MgO spinel refractories have been available for over 30 years. Initially, they were used mainly in Japan and the early formulations had poor properties. Many advances have taken place over time and today the availability of refractories with added spinels and/or magnesia for in-situ spinel formation are numerous and they can be found in many applications.

Although Al_2O_3-MgO spinel refractories were originally developed as a replacement for magnesia chrome, you will seldom find them used as a substitute. Process changes leading to higher temperatures and different slag compositions have changed the environment necessitating the application of more basic refractories.

OTHER

Other spinel compositions are available. Some are undergoing trials and may be considered for use in future refractories, others have been found to be unsuitable for this application and some are not economically worth pursuing.

CONCLUSION

Refractory technology development is a continuous process were one kind of material is replaced by another due to the ever increasing demands of processes, environmental legislation or, raw material availability and cost. In this paper, I briefly reviewed the differing refractory spinel compositions easily available and the changes over time in their usage because of new challenges.

If you have comments about this column or suggestions for future topics please visit me at www.refractoryexpert.com and I will try to address them.

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