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Behavior of Thermbond refractory products under reducing atmosphere

1.) Introduction:

Thermbond refractory products employ a binder system which is based on a neutralization reaction of alkali earth metal oxides with phosphoric acid to stable salts at ambient temperatures. This exothermic reaction leads to flash setting and bodies with high strengths. After setting the resulting body is still acidic because of an excess of phosphoric acid used to mix the material. At higher temperatures above 150°C this acid reacts with alumina to stable aluminium-phosphates. This means the binder system comprises of two independent mechanisms - the alkali-earth metal bond at ambient temperatures, which is an alkali mono-phosphate bond, and a reaction of alumina with an excess of phosphate at elevated temperatures above 150°C to different aluminium-phosphate modifications.

Some literature describes phosphates as not stable in reducing atmosphere above 1550°C or even lower at very low oxygen partial pressures and due to this the industry is sometimes reluctant to install phosphate bonded products in applications like SRU (sulphur recovery units) or hydrogen transfer lines.

In order to evaluate the behavior of Thermbond refractory products under reducing atmosphere *ETV-OES analysis tests (electrothermic evaporation coupled with emission spectroscopy)* have been carried out.

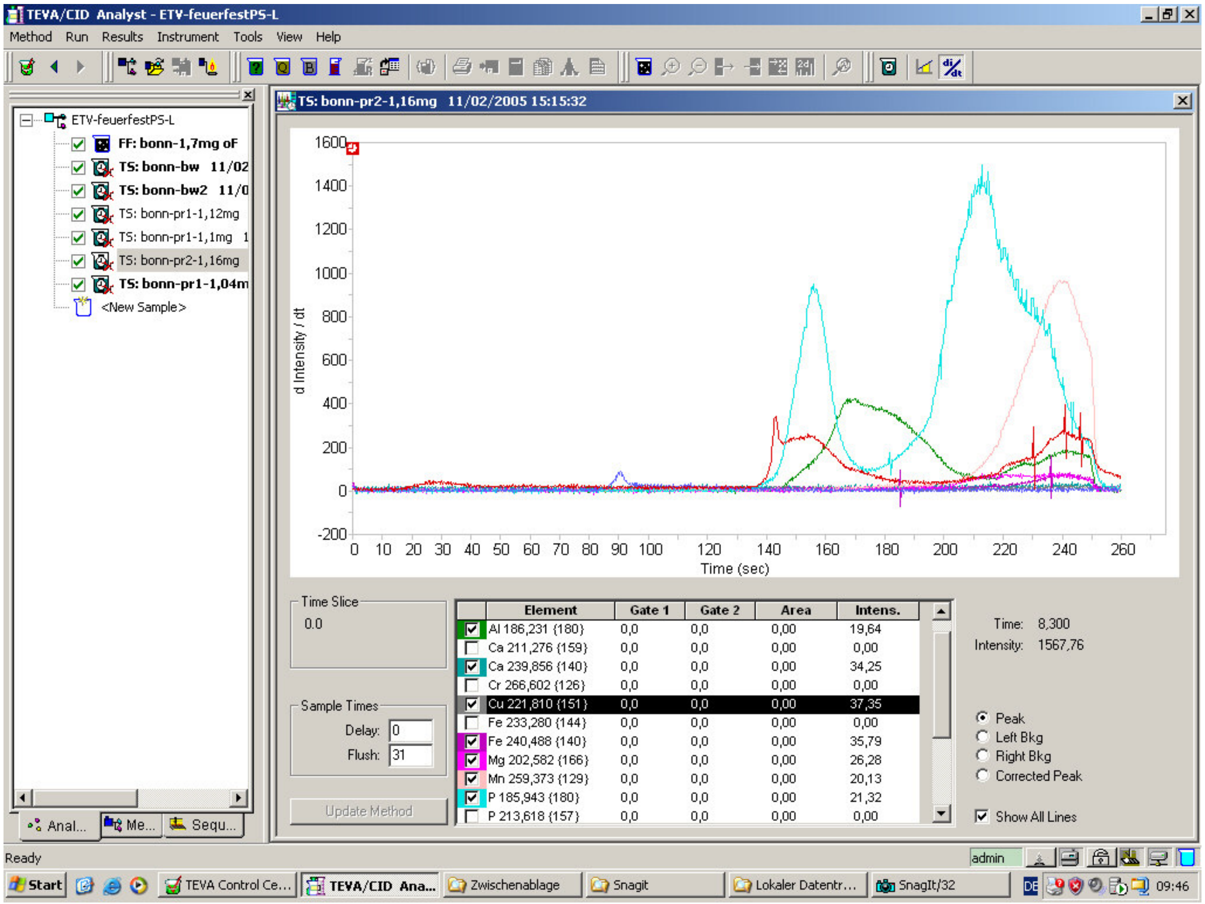
2.) ETV-OES analysis (electrothermic evaporation coupled with emission spectroscopy)

The ETV-OES analysis allows the detection of the decomposition products of oxide compounds during temperature increase and time in reducing atmosphere. The test unit comprises of an electric heated carbon lined furnace chamber and an emission spectroscope unit attached to it. During the test the furnace chamber is purged with argon gas in order to avoid oxygen in the unit.

The test was made with a Formula 5L sample which was pre-fired at 800°C prior testing. The quantity of ground sample material was 1mg. The temperature increase was 100°C / 10 sek.

Therefore the time line is also the temperature line multiplied 10. All tests were carried out at an independent test lab.

2.1) Results and Discussion:



The picture above shows different graphs as the result of the decomposition products of different compounds in the material. The blue graph shows phosphate gas from the decomposition of the different phosphate compounds of the binder system. Since the graph shows two peaks at around 1550°C and 2150°C it is very likely that these peaks represent the aforementioned two binder components. These are:

- at 1550°C aluminium-phosphate. This can be explained by the increase of Al gas (green) in conjunction with the phosphate gas increase.

- at 2150°C calcium phosphate. This can be explained by the slightly increase of Ca gas (green-blue) in conjunction with the phosphate peak at this temperature.

3.) Evaluated data from ETV-OES in comparison with thermodynamic data of the Ellingham- Richardson diagram.

Corrosion Resistance

Corrosion Resistance

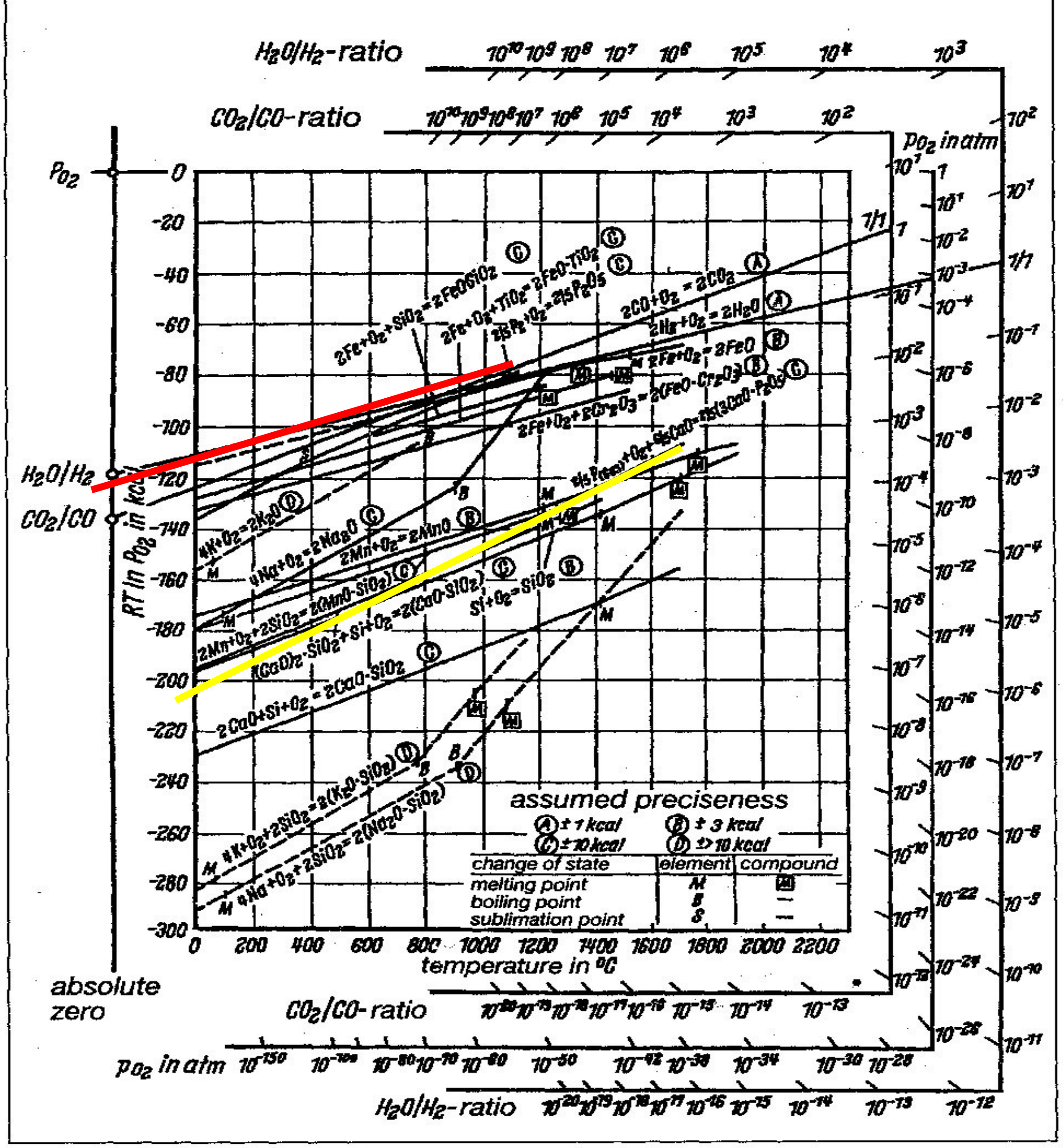


Figure 1: Temperature dependency of reaction temperature in P_{02} values (counts) for some metal oxide compounds (according to F.D. Richardson and J.H.E. Jeffes)

The Richardson diagram describes the reaction/decomposition behavior of different compounds at different temperatures and different oxygen partial pressures. It is obvious that pure P2O5 shows very little stability and decomposes already at relatively high oxygen rates (red line). However, calcium phosphate shows a much higher stability (yellow line). This leads to the assumption that different phosphate compound show probably much higher stability than P2O5.

Unfortunately, there is no diagram data available for mono-calcium-phosphate and mono-aluminium phosphate, which would represent the Thermbond binder components. Therefore a direct comparison of the ETV-EOS analysis with a corrosion diagram is not possible. However, literature describes in different articles (1/2) that mono-aluminium-phosphate decompose to phosphate gas and alumina above 1550°C and this complies with the result of the ETV-OES analysis.

4.) Conclusion

The Thermbond binder system comprises of two binder mechanisms. The primary binder is an alkali earth metal phosphate compound that leads to high strengths at ambient temperatures when formed exothermic after mixing of phosphoric acid with a dry alkali component. The second binder is aluminium-phosphate formed at temperatures above 150°C from additional phosphoric acid and available alumina in the refractory body.

Based on the ETV-EOS testing the two phosphate binders decompose at different temperatures in reducing atmosphere. The second peak occurred at 2150°C and shows very likely the phosphate evaporation of the alkali earth metal oxide compound and it is also conclusive that the first peak at 1550°C is from aluminium-phosphate decomposition, which can be considered as the secondary binder phase in Thermbond. This result complies with literature for aluminium phosphates. It means also that aluminium-phosphates are not stable in reducing atmosphere at temperatures above 1550°C or even lower temperatures if the oxygen partial pressure is significantly further reduced (i.e. vacuum)

The alkali-earth-metal / phosphate compound, however, is stable up to 2150°C which would exceed the operating temperature of SRU's and hydrogen transfer lines by far. It can be stated that based on this test, and over 8 years of successful field applications, Thermbond refractory products resist reducing atmospheres above 1550°C since the primary binder phase, which gives the product its strengths, stays stable up to 2150°C even if part of the binder decompose at lower temperatures.

Firing tests at 3600°C confirmed this result. Test cubes fired in a carbon lined furnace purged with NH2 gas showed no cracking or disintegration.

Literature:

1.) Plicbrico: Refractory Handbook

2.) Alcoa: Monoaluminiumphosphate bonded aluminas