Material solutions for a new process of nutrient recovery by thermochemical treatment of sewage sludge

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Introduction

Phosphorus is an essential plant nutrient and integral component of many fertilizers. Its natural resources are limited and a shortage is previsible with in the next 20 years. A recently developed process [1]. offers the possibility to overcome this problem by recovering Phosphorus from sewage sludge ashes in a two step process that is distinguished by the use of highly chlorine containing atmospheres at temperatures up to 1000°C.

Unfortunately, there are currently no materials commercially available that can withstand such conditions over longer periods of ime.

The aim of the work is therefore to find material solutions for oxygen containing atmospheres with high chlorine contents at extremely high temperatures.

Material Selection and Development

Nickel base alloys

were selected as metallic base material because of their excellent high temperature corrosion resistance. To further improve these qualities, protec ive diffusion coatings had to be designed. The thermodynamic assessment of different coating elements revealed that aluminum and silicon have the best prerequisites to form and maintain slow growing, stable oxide layers. Consequently, Al and Si containing coatings were applied by Pack Cementation. (figure 1)

Ceramic materials

SIC ceramics, as well as **Al_2O_3**, were chosen because of their high hardness and wear resistance combined with exceptional corrosion resistance at high temperatures.

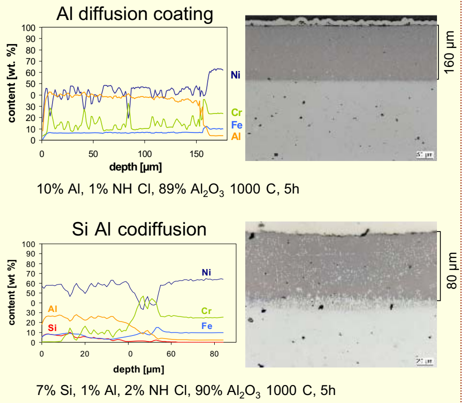

figure 1: Al and Al/Si diffusion coatings on alloy 602CA: quantitative line scan and cross section

Corrosion Experiments

To examine he suitability of the previously chosen materials, long term chlorine corrosion experiments were conducted: They were carried out in a three zone tube furnace at 800 1000°C in synthetic air with 5 and 10% chlorine gas at a flow rate of 4 5 L/h, with the samples in close contact with sewage sludge ashes as will be employed in the industrial process (table 1).

SiO_2	21,6	CaO	15,7
Al_2O_3	10,8	Na_2O	1,04
Fe_2O_3	16,3	K_2O	0,99
MnO	0,15	P_2O_5	21,3
MgO	2,85		

table1: composition of sewage sludge ash [%]

Silicon Carbide Ceramics

Four types of SISC and NSIC ceramics were tested under high temperature oxidizing chlorine corrosion conditions. The results of the corrosion attack on an SISC sample are shown exemplarily in figure 2:

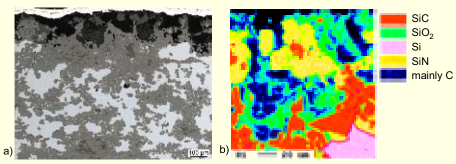

figure 2: corrosion of SISC, *10% Cl_2, 1000°C, 300h*
a) cross-section, b) elemental mapping (ESMA)

The bulk material remains mainly unaffected: It consists of SiC particles evenly distributed throughout a silicon matrix. A loss of Si near the surface can be explained by the following mechanism: During the corrosion process, Si reacts with O_2 to form an SiO_2 layer. This layer forms a eutectic with alkali and iron oxides from the ashes and hereby enables the diffusion of Cl_2. Thus, Cl_2 can reach the pure Si inside the material and the formation of vola ile $SiCl_4$ leads to degradation.

Coated Nickel base alloys

As shown in [2], Al diffusion coatings provide good protection against chlorine corrosion at elevated tempe ratures. This protective effect can be confirmed for aggressive environments of up to 5% Cl_2 in synthetic air at 800°C (figure 3).

At this point, a thin alumina layer forms on top of the coating which protects the alloy from being corroded. Only some minor oxidation of the $Cr_{23}C_6$ precipitates (light phase) can be observed.

figure 3: aluminized alloy 602 CA after corrosion test:
5% Cl_2, 800°C, 300h

Silicon containing coatings though thermodynamically predestined to feature better corrosion protection under the chosen conditions are affected by corrosion phenomena similar to those observed in silicon carbide ceramics. The formation of the previously described eutectic combined with he emission of volatile silicon chlorides accelerates the degrada ion process.

Under extreme conditions (10% Cl_2 in synthetic air, 1000°C, 300h), the formation of a dense protective oxide layer cannot be observed any more. At this point, both types of coa ings have reached their limits.

References

[1] Adam, C., Kley, G. and Simon, F. G., 2007, Mater. Trans., 48 (12), 3056 3061

[2] Bender, R., 2001, Dissertation, RWTH Aachen

Corundum

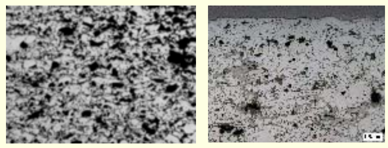

figure 4: Al_2O_3 before (left) and after (right) corrosion test: 10% Cl_2, 1000°C, 300h

The high temperature corrosion resistance of Al_2O_3 was confirmed for oxidizing high chlorine atmospheres: No degradation of the material was detected. (figure 4)

Summary & Outlook

The experiments show that amongst the tested materials, Al_2O_3 is the most suitable for oxidizing high temperature chlorine corrosion conditions followed by aluminized nickel base alloys. SISC and NSIC ceramics suffer the loss of heir silicon matrix and Si containing coatings are heavily attacked, too.

Al diffusion coatings have a great potential to protect nickel base alloys against chlorine corrosion at high temperatures (5% Cl_2, 800°C), although they are not sufficient for extremely harsh environments like 10% Cl_2 at 1000°C.

Although corundum offers outstanding corrosion resistance, its mechanical properties, in particular its brittleness and low thermal shock resistance make it inapplicable as a material for large moving components like rotary furnace tubes. New material solutions have to be developed to combine the chemical resistance of corundum with the mechanical properties of a metal.

Such an approach could be the application of a two layer thermal spray coating system with a ceramic top coat and a corrosion resistant metallic bond coat.