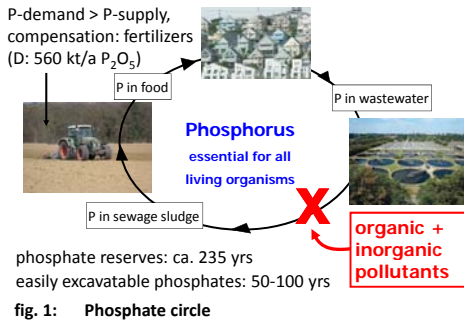


A New Materials Coating Concept for Oxidizing High Chlorine Environments at Elevated Temperatures

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Phosphate recycling



phosphate reserves: ca. 235 yrs
 easily excavatable phosphates: 50-100 yrs
fig. 1: Phosphate circle

To use sewage sludge ash as a fertilizer material, its organic and inorganic pollutants must be removed (fig. 1)

Pollutant removal

EU Project SUSAN → 2-step process:
 1. mono incineration: pyrolysis of organic compounds
 2. separation of heavy metals as heavy metal chlorides (fig 2)

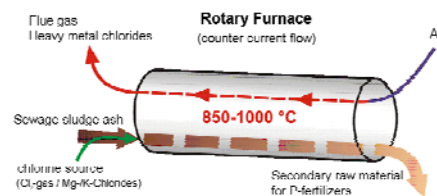


fig. 2: thermochemical process for recovery of phosphorus from sewage sludge ash

A new coating concept

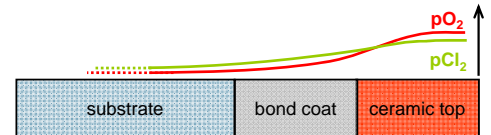


fig. 3: Combination of the erosion-corrosion resistance of corundum with the mechanical properties of an alloy

The coating consists of a two-layer thermal spray coating system with a ceramic top (APS) and a corrosion resistant metallic bond coat (HVOF) especially designed for the use in reducing chlorine environments as can be expected under the ceramic top coat. (fig. 3)

NiAlMo as a bond coat – an alloy for oxygen depleted chlorine environments

Thermodynamic calculations on the resistance of metals under high temperature chlorine corrosion conditions led to the NiAlMo system offering the best protection against chlorine attack, if optimized combinations of these elements are used. β-NiAl with different Mo content was exposed to synthetic air with 10% chlorine gas at 1000°C without pre-oxidation, to investigate the corrosive attack.

By a lower surface reaction rate, the formation of alumina at the surface is promoted. In contrast for pure NiAl all the aluminum transforms into volatile aluminum chlorides and vanishes into thin air. Higher molybdenum contents (>5 at.%) induce a continuous material removal from the surface, because molybdenum forms volatile products, which prevents the formation of a protective alumina layer. Nevertheless the corrosion rate is still much lower than for pure NiAl.

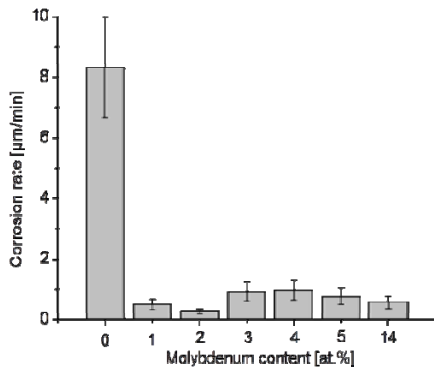


fig. 4: corrosion rate as a function of molybdenum content

Fig. 4 shows that the addition of molybdenum to nickel aluminide highly decelerates the corrosion rate. The lowest corrosion rate was found at molybdenum contents of about 2 at.%. Molybdenum prevents fast depletion of aluminum in the form of volatile chlorides (Fig. 5). The molybdenum surface concentration itself is still low enough to avoid the formation of volatile molybdenum compounds.

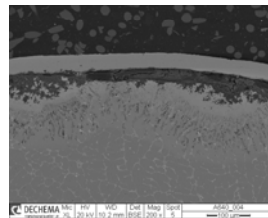


fig. 5: surface of the alloy NiAl+ 2at.% Mo after exposure, a rather dense alumina scale develops at the surface, significantly reducing the corrosion rate.

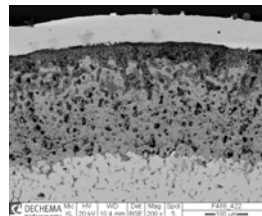


fig. 6: cross-section of the pure NiAl sample after exposure, beneath Ni-chlorides and oxides pure Ni foam is found, as a result of selective extraction of all Al by Cl

Variation of the ceramic top coat

Different ceramics were used as top coat material and tested in chloridizing environments (1000°C, 300h, 10% Cl₂ in synth. air):

Corundum

- low thermal expansion coefficient (7.52 · 10⁻⁶/K)
- phase transformations with large volume changes below 1000°C

Al₂MgO₄-Spinel

- no phase transitions below 1000°C
- thermal expansion as low as Al₂O₃

mixed components (Al₂O₃ : MgO = 7:3)

- expansion coefficient can be adjusted by changing the component ratio

pure MgO

- high thermal expansion coefficient (12-13 · 10⁻⁶/K)
- very difficult to spray – results in low thicknesses
- corrosion resistance still needs to be tested

During the experiments, the NiAlMo layer was very adherent to the substrate (and experienced only minor corrosion with an intact top coat), whereas the ceramic layers showed varying tendencies to spall depending on their thermal expansion coefficients and the amount of phase transformations in the tested temperature range. (fig. 7)

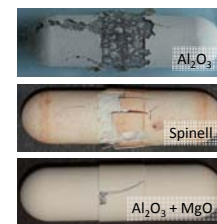


fig. 7: exposed samples spallation effects decrease from Al₂O₃ to pure MgO

References & Acknowledgements

- R. Bender, M. Schütze, *Mat. Corr.*, **54**(9), 652 – 686 (2003)
- H. Latreche, G. Bozzolo, P. J. Masset, T. Weber, M. Schütze, *Mater. Sci. Eng. A*, **527**, 5837 – 5843 (2010)
- H. Latreche, G. Tegeger, G. Wolf, P. Masset, T. Weber, M. Schütze, *Mater. Sci. Forum*, **595-98**(1), 307 – 321 (2008)
- H. Latreche, Dissertation (2009) RWTH Aachen, Germany
- Z. Horita, T. Sano, M. Nemoto, *Acta Metall.*, **34**(8), 1525 – 1531 (1986)
- S. B. Maslennikov, N. N. Burova, V. A. Rodimkina, *Izv. Akad. Nauk SSSR, Met.*, (6), 183 – 190 (1988)

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Conclusions

A new coating design for extremely harsh environments is being developed and its performance can be considerably improved by carefully adjusting coating parameters such as CTE, amount of phase transformations, surface geometry, coating thickness, etc.