Ni-Sn Intermetallics as Inhibitors to Metal Dusting

C. Geers and M. Schütze geers at dechema.de Funded by: AiF Period: 01.07.2007 – 30.09.2009

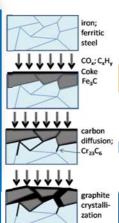


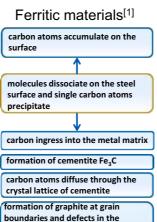
The corrosion resistance of plant components exposed to metal dusting conditions is conventionally achieved by using high-alloyed steels, Ni-base materials or coatings containing high amounts of thermodynamically stable oxide formers such as chromium and aluminium. The protective effect is based on the formation of a continuous, dense and well adherent oxide scale. In the present work a totally different new approach relies on the blocking of the catalytic effect of iron or nickel atoms using tin.

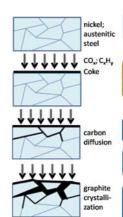
Mechanisms of metal dusting



uncoated low alloy steel (1%Cr; 0.4%Mo) after 100 h under metal dusting conditions at 650°C (H₂-24%CO-2%H₂O)







Austenitic materials^[2,3]

carbon atoms accumulate on the surface

molecules dissociate on the steel surface and single carbon atoms precipitate

carbon diffuses along the low indexed lattice planes

nucleation of graphite at step edges (e.g. Ni(211)) or defects

growth of graphite planes by continuous diffusion of carbon to the step edges

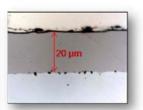
Ni-Sn as an inhibitor for the CO dissociation process on the surface and graphite nucleation in the bulk phase

cementite and at the cementite-meta

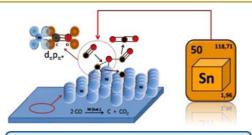
boundary



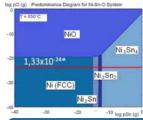
Ni Sn coated low alloy steel (1%Cr; 0.4%Mo) after 100h under metal dusting conditions at 650°C (H₂-24%CO-2%H₂O)



Ni-Sn-coating on low alloy steel (1%Cr 0.4%Mo).



interaction of nickel with CO which catalyses the dissociation and precipitation of carbon



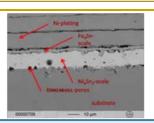
calculated phase stability diagram (HSC 5.0)*p_{O2} in H₂ -24% CO - 2% H₂O (Chemsage)

The new concept is based on the modification of the alloy surface using tin. Tin has the ability to form intermetallic compounds with iron and especially nickel. If a reservoir of nickel ($10\mu m$) is deposited on low alloy steels tin can diffuse into that reservoir and form Ni_3Sn_2 . This Ni Sn phase melts at $1264^{\circ}C^{[4]}$ and is therefore suitable for high temperature applications. The coating remains metallic under metal dusting conditions (see phase stability diagram) in contrast to currently used aluminium or chromium containing alloys. The metallic properties of the Ni Sn scale provide good adherence to the substrate material.

The Ni Sn phase was tested under metal dusting conditions for 2400h without observing any signs of coking or metal dusting. On high alloy steels as well as nickel base materials the deposition of a nickel reservoir is not necessary for diffusing tin into the substrate. For these materials the adherence of the Ni Sn coating is limited by internal oxidation of chromium and therefore less suited to this technique.

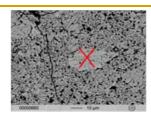


Ni Sn coated low alloy steel (1%Cr; 0.4%Mo) after 2400h under metal dusting conditions at 650°C (H₂-24%CO-2%H₂O). Coking or metal dusting are not observed. Fe₃Sn phase →



After 1000h iron diffused through the Ni Sn phase to the surface and grew a Fe₃Sn layer. Tin itself is not able to diffuse into the low alloy steel material because the atom is too large.

EPMA surface analysis →



EPMA surface analysis: Fe 69; Sn 23; Cr 0.06; Ni 1.4; O 7 at%. The surface looks I ke a solidified melt caused by iron diffusion through the Ni Sn phase.

References

- [1] Natesan et al. 2002 Oxid. Met.
- [2] Abild Pedersen et al. 2006 Phys. Rev. B
- [3] Abild Pedersen et al. 2004 Nature
- [4] P. Nash 1985 Bull. Alloy Phase Diagram

Published

EUROCORR 2008 Edinburgh NACE Corrosion 2009 A lanta EFC Workshop 2009 Frankfurt am Main

Acknowledgment:

This work is financially supported by the German Ministry of Economics via AiF under contract no. 15237 which is gratefully acknowledged.