DECHEMA FORSCHUNGSINSTITUT

Diffusion Coatings for Corrosion Protection of Nickel-Plated Steels for Biomass Combustion Plants

T. Meißner, D. Fähsing, X. Montero, M. C. Galetz | meissner@dechema.de | BMWi via AiF (18370 N) | 1st June 2016 – 30th November 2018

1 Motivation

- Co-firing of biomass increases chlorides and alkali species in steam generator
- Therefore limited to low temperatures and small amounts of biomass

Corroded tubes [1]

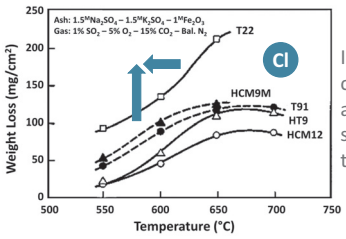
Goal of this study: Development of coatings extending the lifetime of superheater tubes

2 Corrosion Mechanisms

- Formation of eutectic salt mixtures (from alloying elements and deposits)

[2,3,4]	T [°C]	Phases and Eutectics below $(Na,K)_2SO_4$ melting T	T [°C]	Phases and Eutectics below (Na,K)Cl melting T	T [°C]
Na_2SO_4	884	$K_3Fe(SO_4)_3$	618	$FeCl_3$	300
K_2SO_4	1069	$Na_3Fe(SO_4)_3$	624	$KCl\text{-}K_2Cr_2O_7$	368
NaCl	800	$Na_2SO_4\text{-}NiSO_4$	671	$KCl\text{-}K_2SO_4\text{-}Na_2SO_4$	478
KCl	771				

- Dissolution of protecting oxide scales by fluxing mechanisms
- "Active oxidation" by chlorine



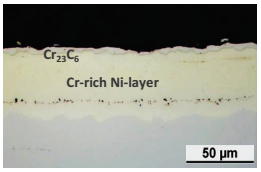
Increase of corrosive attack and shift to lower temperatures

Bell-shaped curve of fireside corrosion [5]

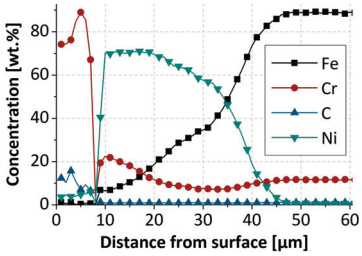
3 Ni + Cr-Diffusion coating

1st step: Interlayer of *electroplated Ni* on X20CrMoV12-1

2nd step: Pack cementation (Cr-powder)



Diffusion coating: 1050°C, 2h (10% Cr, 2% $MnCl_2$)

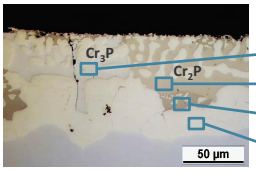


TARGET: obtaining the good corrosion resistance of Ni- and Cr-rich austenitic steel like DMV310N

4 Ni-P + Cr-Diffusion coating

1st step: Interlayer of *electroless Ni plating* on X20CrMoV12-1

2nd step: Pack cementation (Cr-powder)



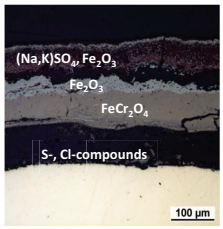
Element	Cr	Ni	Fe	P	C
at.%	44,7	14,2	12,4	22,4	-
	32,3	23,2	8,1	29,8	-
	61,3	1,1	3,6	-	29,2
	19,6	45,1	26,6	1,2	-

Diffusion coating: 1050°C, 2h (10% Cr, 2% $MnCl_2$)

TARGET: same as for Ni + Cr-Diffusion coating, but by using electroless plating → cost-efficient and widely used in industry

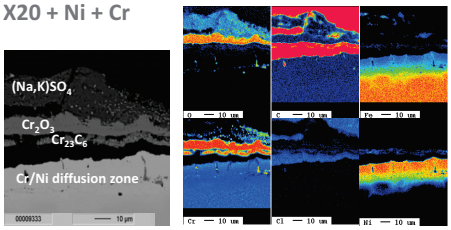
5 Corrosion Test

- 650°C, 100h: HCl- and SO_2-containing atmosphere, slurry-sprayed deposits of sulfates and alkali chlorides (melting point ≈ 600°C)



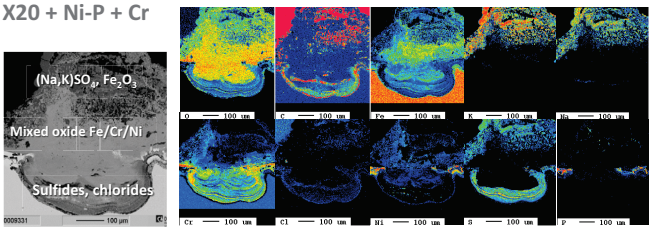
Uncoated X20 reference sample

X20 + Ni + Cr



EPMA-Scan: corrosion resistance notably improved, but detachment from substrate occurs (see also [6])

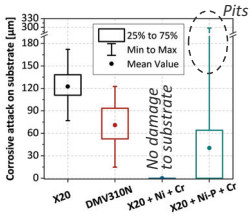
X20 + Ni-P + Cr



EPMA-Scan: coating mostly protective, however local dissolution of phosphides accompanied by pitting observed

Low High

6 Conclusion



Comparison of degradation, 650°C, 100h

- Improvement in corrosion resistance of X20 steel by application of Cr-diffusion coating with Ni-Interlayer
- Cr-carbides are attacked and partly dissolved by chlorine species, but substrate is still enriched in Cr and Ni
- Phosphides from Ni-P interlayer suffer severe corrosion as well

→ **TARGET:** reduction of phosphide-formation by using a low-P containing solution or by replacing P as deposited element

7 Literature

[1] Müller et al. *TK Verlag* (2013)

[2] Bürgel et al. *Springer* (2011)

[3] Niu et al. *Asia-Pacific Journal of Chemical Engineering* (2013)

[4] www.crct.polymtl.ca: PhaseDiagram-Web

[5] Topoda et al. *EPRI Report GS-6422* (1988)

[6] Grabke et al. *Materials Research* (2004)

Supported by:

Federal Ministry of Economics and Technology

on the basis of a decision by the German Bundestag

University of Stuttgart
Institute of Combustion and Power Plant Technology
ifk