Improvement of the Oxidation Behavior of Ferritic-Martensitic Steels in Water Vapor Containing Environments

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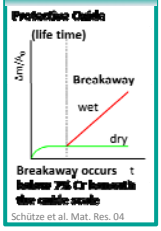
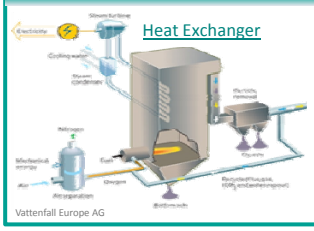
CHALLENGE

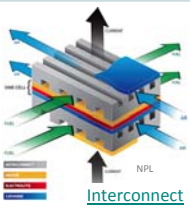


MOTIVATION



Modern heat-resistant ferritic-martensitic steels are of great interest as superheater materials in fossil fuel power plants or as material for interconnects in SOFC's. The environments of such applications contain high amounts of H_2O, which promotes the formation of volatile chromium species $CrO_2(OH)_2$ leading to insufficient oxidation resistance. To apply these steels at temperatures above 600°C new protection systems must be developed:

- co-deposition of Mn and Cr to form a spinel layer during oxidation
- a high Cr-reservoir phase in the subsurface region to avoid early depletion
- enrichment of Co to avoid contamination of the cathode of the SOFC



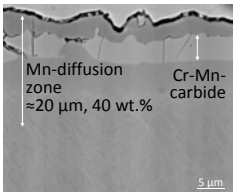
P91

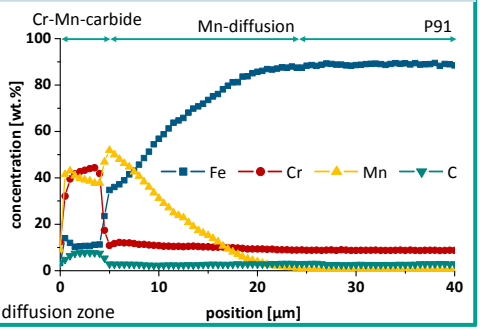
investigated steel

	[wt.%]
Cr	7.9-9.6
Mn	0.25-0.6
Mo	0.8-1.1
C	0.06-0.15

DIFFUSION COATINGS

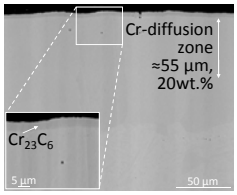
CO-DIFFUSION OF CHROMIUM AND MANGANESE

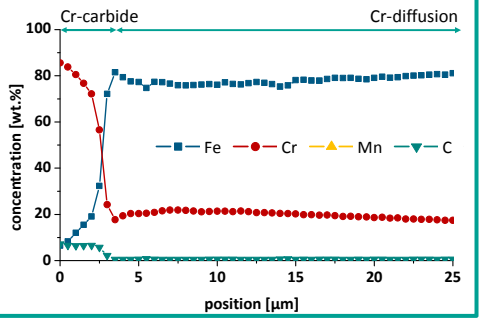




- Powder: Mn, Cr, $MnCl_2$, Al_2O_3, T=1050°C, t=2 h
- Mixed carbide in the enriched zone
- Homogeneous manganese diffusion zone

CHROMIUM COATING



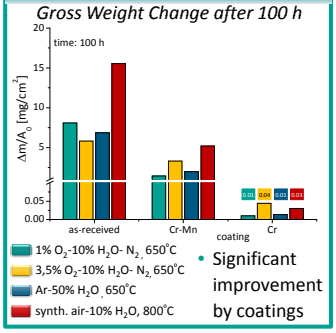


- Powder: Cr, $MnCl_2$, Al_2O_3, T=1050°C, t=2 h
- $Cr_{23}C_6$ layer on surface
- Chromium diffusion zone
- No manganese

OXIDATION EXPOSURE

MASS GAIN

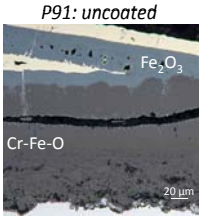
Gross Weight Change after 100 h



- Significant improvement by coatings

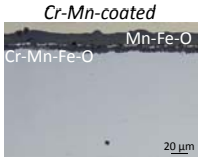
RESULTS AFTER 3000 h IN Ar-50% H_2O AT 650°C

P91: uncoated



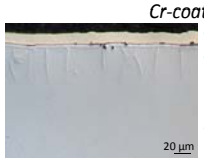
- 150 µm thick
- Chromium depletion beneath the oxide scale

Cr-Mn-coated

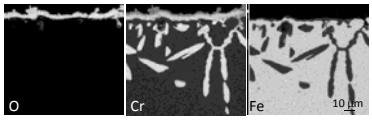


- 20-30 µm thick
- Manganese iron mixed oxide on surface
- No spinel formation
- No spallation

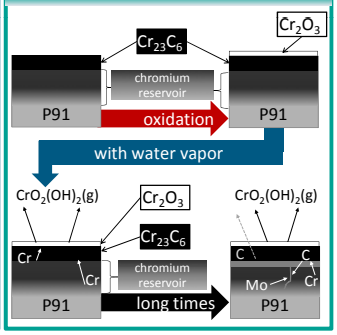
Cr-coated



- 3-6 µm thick
- Carbides below oxide scale at grain boundaries
- Cross contamination with Mn (from other samples)



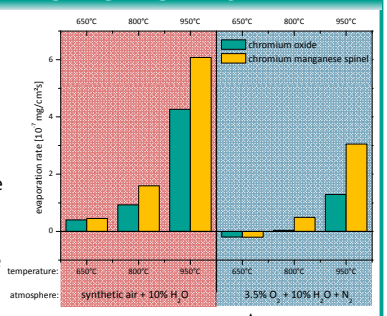
OXIDATION MECHANISM



FUNDAMENTAL INVESTIGATIONS

EVAPORATION RATE OF PURE OXIDES

1. Production of pure Cr_2O_3 and $MnCr_2O_4$ made from metal powder (synthetic air at 1000°C for 50 h)
2. Weighing and determination of volume and porosity by Archimedes' principle and image analysis
3. "Quasi"-isothermal high temperature oxidation exposure in two different water vapor containing atmospheres
4. Gravimetric analysis by microbalance
5. Determination of evaporation rate from mass loss

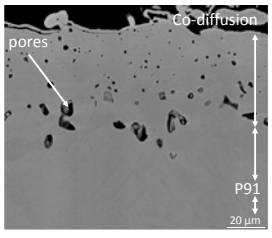


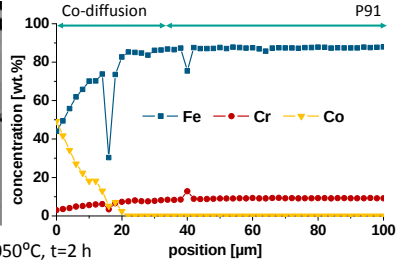
→ **k_v of $MnCr_2O_4$ higher than k_v of pure chromium oxide**

$$\frac{\Delta m}{A} = -k_v t$$

NEW INVESTIGATION FOR SOFC's

DIFFUSION COATING WITH COBALT





- Powder: Co, NH_4Br, Al_2O_3, T=1050°C, t=2 h
- Co content is increased to 50 wt.% to a depth of 20 µm
- Pores have formed due to the reaction and evaporation of Fe with bromine because of the high activity → adjustment is necessary in the new project

CONCLUSIONS

1. Oxidation behavior of P91 was significantly improved in all investigated atmospheres by the developed diffusion coatings.
   → Chromium coating showed best performance.
2. In comparison to pure Cr_2O_3 the evaporation rate k_v of the Cr-Mn-spinel is higher, because of the evaporation of Mn and Cr species from the pure Cr-Mn-spinel.
3. Diffusion coatings with cobalt are possible, but an adjustment of the pack cementation parameters is necessary to avoid evaporation.

ACKNOWLEDGMENT

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