

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

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INTRODUCTION

Modern heat resistant ferritic-martensitic steels are of great interest as superheater materials in fossil fuel power plants or as material for interconnectors in solid oxide fuel cells [1,2].

The environments of such applications contain high amounts of H₂O, which is known to promote the formation of the volatile chromium species CrO₂(OH)₂ leading to insufficient oxidation resistance of 9% Cr-steels in such atmospheres, due to quicker breakdown of the protective chromia layer, the so-called breakaway oxidation [3].

To apply ferritic-martensitic steels at temperatures above 600°C new corrosion protection systems must be developed.

Tab. 1: Composition of steels investigated

wt-%	Cr	Mn	Si	W	C
P91	7.9-9.6	0.25-0.6	0.8-1.1	0	0.06-0.15
P92	8.5-9.5	0.5-0.8	0.5-0.8	1.6-2.0	0.07-0.13

OXIDATION KINETICS

- investigation of Cr₂O₃, Mn₃O₄ and MnCr₂O₄ in 1% O₂, 10% H₂O and N₂ at 650°C
- influence on the kinetics of oxidation
- reference samples from pure metal powder, which were pre-oxidized in synthetic air at 1000°C for 50h

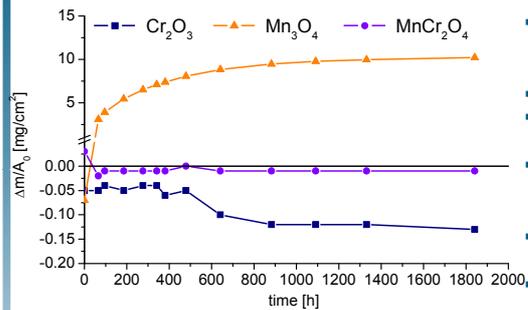


Fig. 1: Weight change of reference samples during oxidation test in 1% O₂-10% H₂O-N₂ (y-axis interrupted)

- Mn₃O₄ was transferred to Mn₂O₃ → great increase of mass during the initial phase of oxidation
- equilibrium is reached for longer exposure times
- mass becomes stable → no evaporation determined in this environment
- corrosion test of Cr₂O₃ in H₂O containing environment result in a mass decrease after time of 450 h
- mass loss can be explained by evaporation of the volatile chromium species CrO₂(OH)₂
- metallic Cr and Mn in a ratio of 1:1 oxidized to (MnCr₂O₄)-spinel phase during pre-oxidation
- spinel shows no significant change of weight in simulated combustion atmosphere at 650°C

DIFFUSION COATINGS

- diffusion coating with **manganese** via pack cementation process
- substrate: P92, powder 5% Mn, 2% MnCl₂, R Al₂O₃, T=1050°C, t=2 h, Ar/ H₂
- uniform diffusion layer with a thickness of around 15 μm
- line-scan of EPMA illustrates the concentration profiles of Mn, Cr and Fe
- Mn is diffused homogeneously into the metal subsurface regions
- no chromium could be detected in the outer coating layer, which is required to form the chromium-manganese-spinel phase

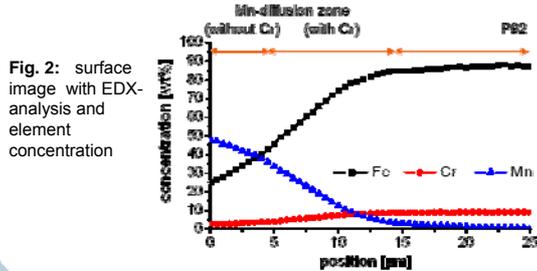


Fig. 2: surface image with EDX-analysis and element concentration

- diffusion coating with **chromium** via pack cementation process
- substrate: P92, powder 10% Cr, 5% MnCl₂, R Al₂O₃, T=1050°C, t=2 h, Ar/ H₂
- chromium carbide layer on surface (thickness: ~5μm)
- chromium enriched zone underneath with a depth of around 75 μm
- no manganese was detected
- in chromium enriched zone large ferrite grains had developed, that do not have a negative influence on the mechanical properties of the bulk material, because they are only present in the metal subsurface region

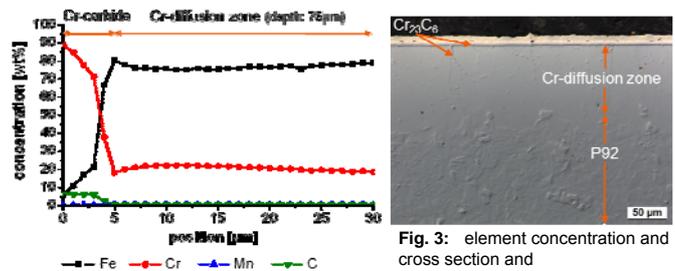


Fig. 3: element concentration and cross section and

OXIDATION BEHAVIOR

oxidation experiments in simulated combustion environment with 1% O₂, 10% H₂O and N₂ at 650°C

Manganese Coated Sample

- oxidation rate is initially very high, subsequently rate decreases significantly, no spallation in crucible
- formation of rapidly growing surface manganese oxides, however kinetics of further oxidation is very slow (see reference oxides on top) → evaporation of CrO₂(OH)₂ inhibited

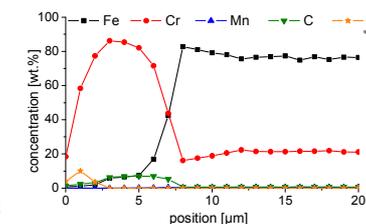


Fig. 5: element concentration of oxidized chromium coated sample (P91)

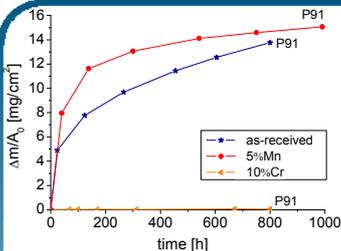


Fig. 4: weight change vs. time (1% O₂, 10% H₂O and N₂, T=650°C)

Chromium Coated Sample

- surprising kinetic stability
- formation of thin Cr₂O₃-scale on chromium carbide
- underneath chromium enriched zone even after 800 h of exposure
- Fig. 6 illustrates the development of Cr-concentration for long oxidation times

CONCLUSION AND OUTLOOK

The improvement of oxidation behavior of ferritic-martensitic steels could be demonstrated.

The formation of a chromium-manganese-spinel surface on the substrate during high temperature exposure has not been successful yet due to the "low" temperature of 650°C.

The spinel formation starts at temperatures above 800°C. Therefore further samples will be coated with different powder compositions and afterwards a pre-oxidation at 1000°C will be executed.

For application of ferritic-martensitic steels e.g. in SOFCs with other compositions and elements (e.g. Co) will be developed. These samples have to be investigated in oxidizing atmospheres above 800°C.

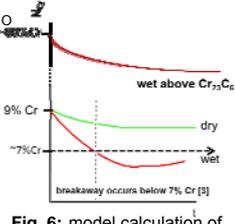


Fig. 6: model calculation of minimum Cr-concentration to form Cr₂O₃ scale at 650°C [3]

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