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 Cr₂O₃(OH)₂ leading to insufficient oxidation resistance of 9% Cr-steels in such atmospheres, 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.

OXIDATION KINETICS
- investigation of Cr₂O₃, MnO, 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
- Mn₃O₄ was transferred to Mn₅O₇ → 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 Cr₂O₃(OH)₂
- metalic 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

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.

REFERENCES

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