Karl-Winnacker-Institut High Temperature Materials

Behaviour of NiAlMo APS-coatings in chlorine-based environments

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Introduction

Corrosion by chlorine at high temperature is a serious problem encountered in energy conversions, chemical and metallurgical industries, e.g., coal-fired boilers, waste incinerators and plastic/polymer decomposi ion mills.This chlorine corrosion process is well-known as **"active oxidation"** (Fig. 1). It leads to a catastrophic attack and needs to be limited. Corrosion resistance of materials at high temperatures in oxidizing atmospheres is usually obtained by the formation of a protective surface oxide scale. Under chloridizing conditions the situation is much more complex. The protective scale formation may be considerably affected by the presence of chlorine.

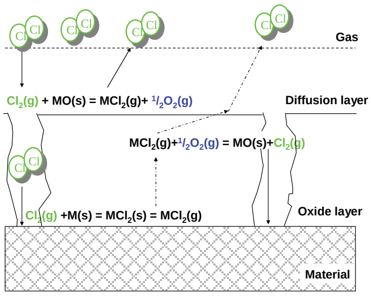

Fig. 1 Corrosive attack of materials in chlorine environment "active oxidation process" [1].

A new type of diagrams (Fig. 2) where the rate of thickness loss of different elements was introduced as a criterion to dis inguish between protective and corrosive range, has been developed [2]. These diagrams take into account the mass transfer kinetics and thermodynamic considerations.
The line for each element separates the protec ive zone (below) and the non-protective zone above. Molybdenum seems to have a positive behaviour in "reducing"-chloridizing atmosphere, whereas aluminium has a positive behaviour in "oxidizing"-chloridizing atmosphere. For this reason,NiAlMo APS–coatings were developed and tested in chlorine-based atmospheres with low oxygen level. The exposed samples were then analyzed by optical microscopy and EPMA.

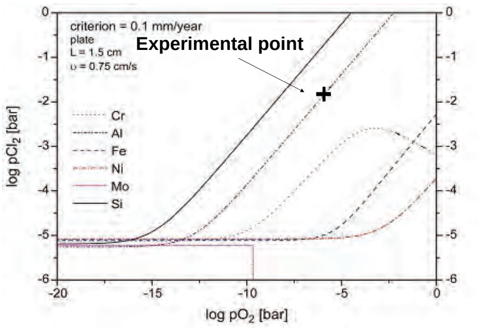

Fig. 2: "Quasi-Stability" diagram of Al, Fe, Cr, Ni, Mo and Si as a function of Cl_2 and O_2 contents at 800°C [2].

Experimental procedure

NIAlMo APS-coatings were applied on cylindrical Armco iron specimens. The behaviour of the coatings was studied under chloridizing atmosphere with low oxygen level at 800°C for 300 h.

Coatings characterization

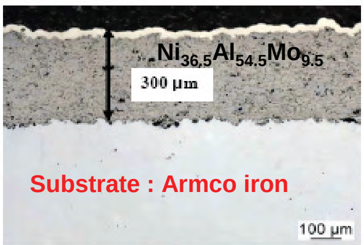

Fig. 3: Cross section image of a NiAlMo APS-coating.

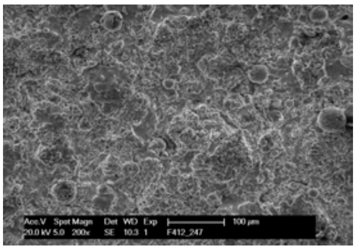

Fig. 4: SEM image of a NiAlMo APS-coating surface.

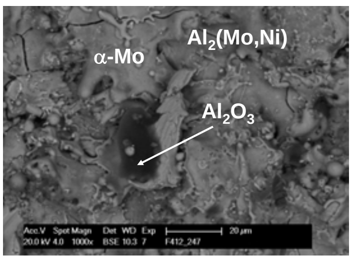

Fig. 5: SEM contrast phase image of a NiAlMo APS-coating surface.

Heat Treatment

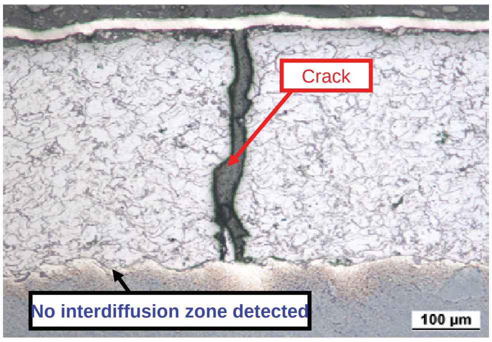

Fig. 6: Cross section image of a NiAlMo APS-coating under Ar at 800°C, 100h.

No interdiffusion zone was detected by SEM analysis. Nevertheless a crack due to the high amount of alumina in this coating was observed, which occurred probably during he cooling.

Cl_2 corrosion test

- **Ar-1% Cl_2 -3 ppm O_2, 300 h**

Optical microscopy

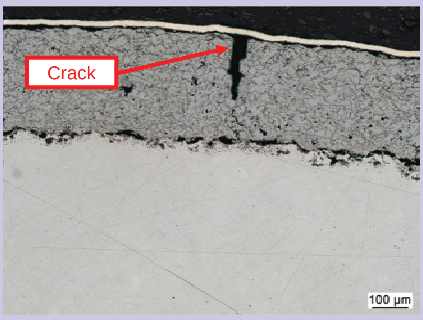

Fig. 7: Cross section image of NiAlMo APS-coating, 800°C, 300 h, Ar-1 % Cl_2- 3 ppm O_2.

Cl_2 corrosion test

- **Ar-1% Cl_2 -3 ppm O_2, 300 h**

Elemental mapping

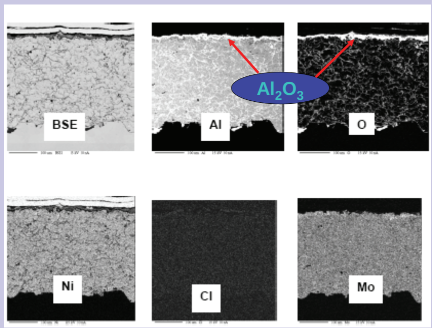

Fig. 8: Elemental mapping of NiAlMo APS-coating, 800°C, 300 h, Ar-1% Cl_2- 3 ppm O_2.

A very thin and compact alumina scale was detected. The high resistance of this coa ing may be explained by the high amount of he α-Mo phase and Al_2O_3 which showed a very high stability under chlorine atmospheres. However, internal oxidation was also observed which causes some delaminations and cracks during cooling.

Conclusion

The formation of an α-Mo phase in NiAlMo APS-coatings leads to a high resitance against chlorine attack. The aluminium rich $Al_2(Mo,Ni)$ phase provides however internal oxidation and causes cracks. It should be interesting to produce the same coating but in by the HVOF process to avoid the extremely high amount of alumina.

References

[1] R. Bender, M. Schütze ; Materials and Corrosion, 54, (2003) 567-586.

[2] S.Doublet ; Doctoral Thesis, RTWH Aachen, 2006.