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Development of a new out-of-pack diffusion coating treatment for high corrosion resistance of steam power plant materials

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INTRODUCTION

Modern 9-12% Cr ferritic-martensitic steels are used in conventional power plants for steam lines, boiler piping, superheaters and steam turbines. To improve the efficiency of power plants, supercritical steam parameters up to 650°C and 300 bar are required. The martensitic steels show good mechanical properties under these conditions but the corrosion resistance should be improved. Austenitic steels and nickel-based alloys are potential candidates for increasing the steam temperatures up to 700°C.

In order to protect the martensitic steels the diffusion process has to fit the substrate requirements concerning the process temperature and time. Indeed, above a certain temperature, the martensite transforms into ferrite and the material thus looses its mechanical strength. For P91 martensitic steels the martensitic-ferritic phase transition occurs at 650°C. As a consequence, a new low temperature out-of-pack process will be developed. The process enriches the substrate surface with elements that are expected to form a protective oxide layer under service conditions. These elements are: Mn, and Si and a combination of both, which are introduced at high temperature by diffusion into the substrate surface.

A high Mn content in the surface zone forms protective MnCr-spinels. Si is expected to form a diffusion barrier, which could reduce the Cr diffusion into the oxide scale. A diffusion coating with both elements should produce a synergetic effect.

SUBSTRATE MATERIAL

Samples of Cr steels are cut to 20 x 9.5 x 3mm.

Fig. 1: Sample of Cr steels

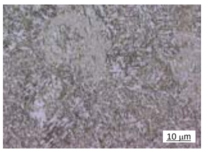


Fig. 2: Microstructure of martensitic steels

	P91	HCM12A	Nf616 (P92)	E911
C	0,06-0,15	0,07-0,14	0,07-0,13	0,1-0,13
N	0,025-0,08	0,06	0,03-0,07	0,05-0,08
Si	0,18-0,56	<0,5	0,04	0,1-0,3
Cr	7,9-9,6	10,0-12,5	8,5-9-5	8,5-9,5
Al	<=0,05	<0,04	<0,04	0
Ni	<=0,43	0,28-0,34	0-0,4	0,2-0,4
Mn	0,25-0,6	0,54-0,63	0,3-0,6	0,3-0,6
Mo	0,8-1,1	0,25-0,6	0,3-0,6	0,9-1,1
V	0,16-0,25	0,15-0,30	0,15-0,25	0,15-0,25
Nb	0,05-0,11	0,09-0,10	0,04-0,09	0,06-0,1
W	0	1,5-2,5	1,5-2,0	0,9-1,1
others				
Co	0,01			
P	<=0,025	<0,02	<0,02	
B	0	<0,005	<0,02	<0,006
Cu		0,3-1,7		

Table 1: Composition of Cr steels (wt%)

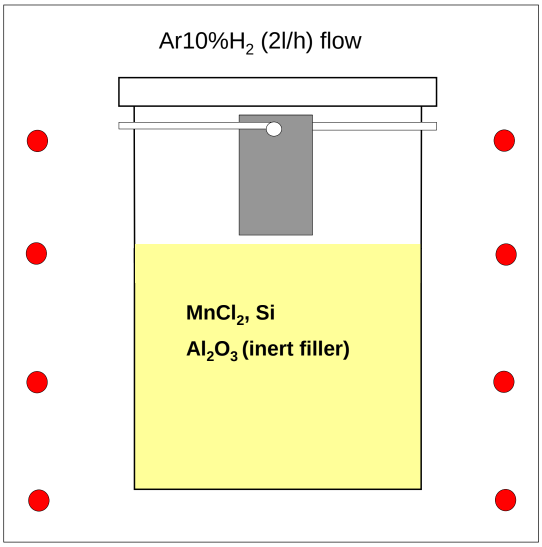
CO-DIFUSSION TREATMENT

Enrichment of Mn and Si in the surface zone should produce a synergetic effect to improve the corrosion resistance of Cr-steels. Due to the different properties of Mn and Si in forming chlorides a compromise between high $MnCl_2$ and $SiCl_4$-activitiy and moderate temperature must be found.

EXPERIMENTAL PROCEDURE

For the new out-of-pack process the specimens are hung over a powder mixture composed of a masteralloy ($MnCl_2$ or Si) and an inert filler (Al_2O_3). Powder mixture and specimen are sealed in a crucible. The crucible is placed in a tubular furnace. A Ar-5%H_2 (2 l/h) flow is passed through the furnace while it is heated to the desired temperature. Once the temperature is reached, the flow is stopped in order to retain the Mn-Chloride vapour. For the Mn coating process temperatures over 1000°C are needed.

furnace



Characterisation: After the treatment the samples were electroplated with nickel before cross sectioning, polishing and analysing by light microscopy, SEM-EDX.

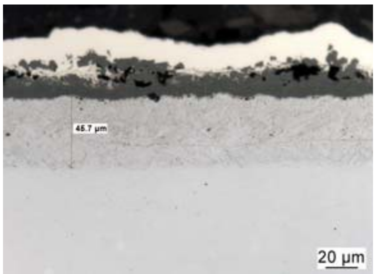


Fig.3: cross-section of nitrogen diffusion layer

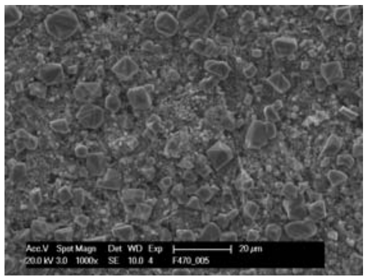


Fig.4: octahedral spinel crystals on the surface

RESULTS

The aim is to develop a new out of pack diffusion coating process to produce homogenos Mn-difusion-layers. If NH_4Cl is used as an activator, nitrogen diffusion layers are formed. Mn is enriched in the surface zone to 5-10 wt%. During the treatment small Mn-spinel crystals are grown on the coating surface. So far it is not possible to avoid growing of these Mn-rich oxides. The high Mn content is the basis to form corrosion resistance oxide layers in steam atmosphere under service conditions.