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High temperature corrosion in modern thermal power generation: gas turbines, high efficiency boilers, IGCC

N. Bolt

N.V. KEMA, P.O. Box 9035, 6800 Et Arnhem, The Netherlands

Abstract. — In coal fired low NO_x boilers under mild reducing conditions the use of a CrV-diffusion coating on stabilized 10CrMo9.10 is promising. For super heaters in oil fired super critical units, the coextruded materials with 35Cr and 46Cr are suited. For IGCC conditions coextruded 310 material is probably suitable as water wall material and 26Cr41Ni3V as super heater material.

1. Introduction.

The total power capacity in the Netherlands today amounts to about 15 000 MWe. From which 10 000 MWe is natural gas fired, about 4 000 MWe coal fired and about 500 MWe nuclear based. In the last decade gas fired units have been retrofitted with gasturbines, with machine capacities ranging from 100 to 150 MWe. Experience with failure causes and repair methods was obtained in that period. In this decade twelve modern gas fired combined cycles (efficiency 55% LHV) and cogeneration units will be constructed. Gas turbine machine capacities of 200 MWe are involved. Most of the coal fired units are special designed for or retrofitted with low NO_x burning techniques. Two super critical 600 MWe blocks with efficiencies of 42% (LHV) are under construction. Full scale Integrated Gasification Combined Cycles are scheduled to start up from the end of this century on. A 250 MWe IGCC demonstration plant will be put in operation in 1993 at Buggenum with a efficiency of 43% (LHV).

2. High temperature corrosion R and D.

In the light of the above mentioned developments, KEMA an independent organization with R and D, testing, certification, engineering and consultancy activities in the field of the electric power supply has set up a research program on the selection of materials including background mechanisms for:

- repair of gasturbine vanes and blades;
- repair of low NO_x water wall tubes in coal fired units;
- use in super critical high efficiency boilers;
- use in first and second generation IGCC.

3. Gasturbines.

In a gasturbine air is compressed, mixed with gas and burned. The flue gases enter the expander at a (nowadays) inlet temperature of 1100 °C and enter after expansion a waste heat boiler at about 550 °C. Especially the first stage turbine blades suffer from both heat load and corrosion. The blades have got a heat pretreatment at about 850 °C. The operation temperature is in the same range resulting in structure changes during operation. Structural changes as a function of time and temperature form part of the ongoing project. Corrosion has been primarily described to the aggressive action of sodium sulphate and chloride salts. In the coastal and industrial areas the air contains sodium chloride aerosols and sulphuroxides. Especially during humid periods concentrated spots on the air filter are blown in. The molten (mp. $\text{Na}_2\text{SO}_4 \cdot \text{NaCl}$ 630 °C) salts have caused severe corrosion problems. The turbine materials consist in general of nickel or cobalt based alloys. In the nickel based alloys about 10-20% Cr is present for enhanced sulphidation resistance and about 5% Al for strength and oxidation resistance. In the Co-based alloys the Cr-content is higher 20-30%. Because of chromium reduces the amount of the (strengthening) γ -phase its content in the super alloys is limited. Actual used materials are represented in table I.

Table I. — *Actual used gasturbine materials.*

component	material	Ni	Co	Cr	W	Mo	Al	Fe	Ti	others
blades	IN738 LC	bal	8.5	16	2.6	1.75	3.4	0.5	3.4	1.75 Ta
guide vanes	FSX 414	10.5	bal	29.5	7	-	-	≤2	-	<1 Si, Mo
housing	IN 617	bal	12.5	22	-	9	0.3	1.5	1.2	0.2 Cu

Repair procedures have been developed consisting of profile reshaping, heat treatments and applying improved coatings. For instance at a damaged blade of IN 738 LC with an original vapour sprayed coating of CoCrAlY an improved coating with an alumina diffusion layer was applied.

4. High efficiency boilers.

4.1 AT LOW NO_x BURNING TECHNIQUES. — the main idea is the further staging of the air supply and the separation of the flame in a fuel rich primary zone and a burning out zone where the remaining air is supplied. In general some excess air is supplied with respect to the stoichiometric burn out of the fuel. Under low NO_x -firing conditions locally reducing circumstances occur near the water wall tubes, resulting in the presence of CO and H_2S . Values of 1-5% CO and up till 0.1% H_2S have been measured in a demonstration program. From the Fe-O-S stability diagram in figure 1a it can be seen that already at an air/fuel-ratio of 0.9 FeS tends to be a stable compound while chromium (Fig. 1b) forms stable oxides. At normal firing conditions (metal temperature 400-450 °C, flue gas temperature about 1400 °C) low alloyed steel types are used like 10Mo3, 13CrMo4.4, 10CrMo9.10. Candidate materials

Fig. 1. — a) Stability diagram of the Fe-S-O system at 475 °C; b) Stability diagram of the Cr-S-O system at 475 °C.

with a higher sulphidation resistance have been tested. A part of some ferritic and austenitic steels, protecting layers have been examined which could easily be applied on (existing) low alloyed water wall tube sections. The project has been performed in a national program in which the government (NOVEM), universities (UT, TUE), the industry (Interturbine) and technical institutions (KEMA, TNO) were involved [1]. A selection of the materials examined is given in table II.

The samples have been tested on coating stability (450 °C vacuum, 8000 h), corrosion (general attack; 500-1500 h in sulphidizing gas at 450 °C, shut down attack: alternatively 80 h at high temperature and 50 h at 45 °C in humid atmosphere) and mechanical properties (*via* Constant Extension Rate Techniques and Low Cycle Fatigue tests). Examples of cross sections after simulation of shut down attack and CERT experiments are represented in figures 2a and 2b. A final judgement based on these tests has been made and is represented in table III.

It was concluded that the reference materials 15Mo3, 13CrMo4.4 and 10CrMo9.10 showed an unacceptable resistance to sulphidation and shut down corrosion. The ferritic material 446 is corrosion resistant due to the high chromium content, but the rupture/extension ratio is relatively low. Although the 310 material seems to be sensible for intercrystalline corrosion, the overall impression is positive. The Cr- and CrV-diffusion coatings on Nb stabilized 10CrMo9.10 behave well. Because of intercrystalline shut down corrosion phenomena in the Cr-diffusion coating, the CrV-coating seems to be the best choice. Promising materials will be tested during the period 1992-1994 in the KEMA 1 MW th coal fired plant.

4.2 HIGH EFFICIENCY BOILERS. — are a.o. characterized by their super critical steam conditions resulting in a need for stronger super heater tube materials operating at higher metal temperatures (600-700 °C). A test program for oil fired conditions has been completed, for coal fired conditions been started. To meet the demands of super critical steam pressure re-

Fig. 2. — a) Cr- and CrV-coatings after shut down attack simulation. The CrV-coating (12-5) is not damaged, the Cr-coating (13-5) is intercrystalline attacked; b) Coatings after CERT experiments. The CrV-diffusion coating (RB 56) shows superficial cracks, the plasma-sprayed coating (RB 57) is frequently cracked and separated from the substrate.

Table II. — *Reference and examined low NO_x water wall materials.*

material		Cr	Ni	Mo	Mn	Si	other
15Mo3		—	—	0.3	0.6	0.3	—
13CrMo4.4		0.9	—	0.5	0.5	0.2	—
10CrMo9.10		2.3	—	1.0	0.5	0.3	—
Tp 446		26	0.3	—	0.2	0.5	N
AISI 310		24	20	—	1.8	1.3	—
diffusion coating	substrate						
Cr	15Mo3	50					
	10CrMo9.10	58					
CrV	15Mo3	20					V
	10CrMo9.10	43					V

Table III. — *Lab tests based selection of materials for water wall tubes in low NO_x conditions.*

material	coating stability	corrosion general/shut down	CERT	LCF	overall
Tp 446		+	—		+/-
AISI 310		+	—	+	+
Cr diff.15Mo3	—	+	+	+	—
Cr diff.10CrMo9.10	+	—	+	+	—
CrV diff.15Mo3	—	+	+	+	—
CrV diff.10CrMo9.10	+	+	+	+	+

sistance inside and sulphidation resistance outside, coextruded materials were selected with inside a strong and outside a high chromium-containing alloy (25-50% Cr). As a reference the conventional monobloc material AISI 347H was chosen. The materials (see Tab. IV) were exposed in cooled probes in the flue gases of the heavy oil fired 3 MW th pilot plant of KEMA.

Metal temperatures are presented in figure 3a. It can be concluded that with increasing chromium content, the corrosion resistance at metal temperatures between 600 and 700 °C increases as well [2]. In the critical temperature range of 630-675 °C, where a liquid phase at the metal/deposit interface is present, the alloys Inconel 671 and NAC 35CrA behave extremely well under continuous and discontinuous load and at flue gas temperatures of 1000 and 1125 °C. In addition the ferritic steel 446 seems also to be sufficient corrosion resistant under these conditions. Analysis of the deposit build up revealed that at metal temperatures between 630 and 670 °C a sodium-, calcium-, iron-, sulphate layer is present in the first

100 μm from the metal/deposit interface. With DSC-DTA measurements [2] it was demonstrated that:

Table IV. — (Coextruded) materials tested in the oil fired KEMA boiler.

inside/outside	manufacturer	% Cr	% Ni	% Si	% Mn	% Mo	% Nb	% Cu	% C	% P	% S
AISI 347H	Sandvik	18,2	9,8	0,57	1,16	-	-	-	0,04	0,012	0,010
E.1250/310	T.I.	15,1	9,2	0,55	5,9	0,96	0,88	-	0,12	0,025	0,014
		25,5	20,2	1,22	1,23	-	-	-	0,07	0,024	0,005
800H/Tp.446	Sandvik	20,8	31,1	0,43	0,56	-	-	0,03	0,07	0,008	0,003
		26,4	-	0,44	0,88	-	-	-	0,19	0,021	0,003
1714CuMo/35CrA	Nippon Kokan	15,3	14,5	0,54	0,75	2,42	0,40	2,96	0,12	0,021	0,001
		35,1	45,5	0,03	0,02	-	-	-	0,05	0,002	0,001
800H/671	Inco	20,0	31,2	0,42	0,92	-	-	0,04	0,11	-	0,002
		47,3	52,7	-	-	-	-	-	0,05	-	-

- $\text{Fe}_2(\text{SO}_4)_3/\text{Na}_2\text{SO}_4/\text{CaSO}_4$ mixtures are liquid from about 630 °C;
- $\text{Fe}_2(\text{SO}_4)_3$ decomposes in Fe_2O_3 and SO_3 with a maximum rate at 675 °C at which temperature the remainder $\text{Na}_2\text{SO}_4/\text{CaSO}_4$ recrystallize.

For this critical temperature range, where the maximum corrosion occurs the inward sulphur and oxygen transport reactions and the outward iron-, nickel- and chromium transport reactions are presented in figure 3b. It has been assumed that the supply of oxygen and sulphur (as SO_3) to the interface oxide-melt is the rate determining transport reaction. The transport of SO_3 through the molten sulphate layer is diffusion-controlled and occurs according to Ficks's first law:

$$J_{\text{SO}_3} = -D \cdot \Delta P_{\text{SO}_3} / X$$

D = diffusion coefficient in molten sulphate

X = thickness of the molten sulphate layer

$$\Delta P_{\text{SO}_3} = P_{\text{SO}_3} (\text{melt/oxide}) - P_{\text{SO}_3} (\text{melt/ash})$$

The flux of SO_3 through the molten sulphate layer could be calculated in this way as a function of the metal temperature [2]. In figure 3c this relation is represented. It can be seen that both SO_3 -flux and corrosion rate increase rapidly with increasing metal temperatures. Above 671 °C, $X = 0$ and the transport processes are governed by solid state diffusion: the corrosion rate drops then sharply.

5. IGCC.

Materials in the reactor and radiant/convection coolers at entrained bed gasifiers suffer from very aggressive conditions. Material tests under these conditions are performed in order to select materials both for service and repair at actual conditions and at near future conditions with higher metal temperatures. KEMA is involved in several test programs: at the SAR plant in Holten Germany. Participants are Ruhrchemie AG, Ruhrkohle AG, Deutsche Babcock, Man./GHH, Stork, EPRI and KEMA. At the test program in the PRENFLO-plant in Fürstenhausen (Germany) during 1992 (participants PRENFLO, EPRI and KEMA) and at

Fig. 3. — a) Corrosion rates of 347H, 310, 446, Cr35A and 671 at oil fired conditions of the 3 MW th pilot plant at KEMA. b) Proposed transport reactions in the presence of a molten sulphate layer (t_{metal} : 630-675 °C). c) Calculated SO_3 fluxes (dashed line) in the deposition layer as a function of the metal temperature.

Fig. 4. — a) Calculated temperature distribution in one of the finned test probe. b) Corrosion rate of low alloy ferritic steels under gasification conditions; c) Schematic representation of the attack mechanism at Down Time Corrosion simulation of Cr-, CrV-coatings in a gasifier. Stage 1 attack up till substrate. Stage 2 severe substrate attack.

the 250 MWe IGCC in Buggenum during 1993-1996 (participants Sep, Demkolec, KEMA). In the SAR project [3] eight steam cooled high temperature test loops are installed in the radiant cooler. The metal temperatures ranged, in order to simulate evaporator conditions, from 400-450 °C and to simulate super heater conditions from 512-570 °C. In figure 4a a schematic view is given of the calculated temperature distribution in one of the finned test probes. Low alloyed boiler steels (with and without chromized coatings), austenitic stainless steel and high nickel alloys were exposed. The raw syngas composition contained 0.2% H_2S , 42% CO and probably 400-800 ppm HCl and further H_2 , CO_2 , H_2O , N_2 , CH_4 . The total ex-

posure time was about 3600 hours during which seven shut downs occurred. The test results demonstrated that the low alloyed boiler tubes suffer from unacceptable high corrosion rates caused by sulphidation possibly accelerated by chlorination. Vanadium modified chromium diffusion coatings on stabilized alloys are less subject to pitting and intergranular corrosion than previously tested chromium rich coatings. Coating failures can still be expected however after 10-20 000 hours of operation. Austenitic steels like AISI 310 tend to form thin protective scales at evaporator tube temperatures and are, in coextruded form on low alloy ferritic steel tubes, promising candidates for water wall tubes. An experimental alloy 26Cr, 41Ni, 3V formed a thin continuous protective Cr_2O_3 scale with $\leq 1\%$ sulphur in it during exposure at metal temperatures higher than 500 °C and offer perspectives for use as super heater tube material.

Down time corrosion contributes to the overall corrosion rate of the materials in the gasifier and coolers: during down time periods the hygroscopic sodium- and iron chlorides in the deposits attract water, resulting in a very corrosive medium near which (electrochemical) corrosion reactions can occur. A series of Cr- and CrV-coatings have been screened with a DTC test, developed by EPRI [4]. In this case a mixture of coalash/ FeCl_2 / NaCl in the ratio 90/6/4 was used. A classification of increasing resistance to DTC was obtained going from I to V:

- I) Cr- and CrV-coatings on St.35 15Mo3 and Cr-coating on 10CrMo9.10;
- II) Cr-coating on HR3C and CrV-coating on Inconel 800H;
- III) CrV-coatings on 10CrMo9.10;
- IV/V) Cr- and CrV-diffusion coatings on Nb stabilized 10CrMo9.10 and 9Cr1Mo.

The attack varies from mild surface attack *via* pitting corrosion to intergranular attack. The last situation is schematically represented in figure 4c.

6. Conclusions.

Concerning modern 150-200 MW gasturbines a growing need has been signaled for (blade) repair aspects available for the users of these machines.

About conventional coal fired boilers, equipped with low NO_x firing techniques, it was found that for repair purposes a CrV diffusion-coating on stabilized 10CrMo9.10 is promising. For super critical units it is concluded that under oil fired conditions the coextruded materials 1714CuMo/35CrA (inside/outside) and 800H/671 will be suitable as superheater materials.

From tests under coal gasification conditions in practice it appeared that coextruded material with 310 outside is probably suitable for use as water wall tube and the material 26Cr41Ni3V probably as superheater material.

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