Oxidation performance of high temperature steels and coatings for future supercritical power plants

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Abstract

The operating efficiency of current and future thermal power plants is largely dependent on the applied temperature and pressure, which are in part limited by the internal oxidation resistance of the structural materials in the steam systems. Alternative and reference materials for such systems have been tested within the COST 536 (ACCEPT) project, including bulk reference materials (ferritic P92 and austenitic 316 LN steels) and several types of coatings under supercritical combined (oxygen) water chemistry (150 ppb DO) at 650ºC/300 bar. The testing results from a circulating USC autoclave showed that under such conditions the reference bulk steels performed poorly, with extensive oxidation already after relatively short term exposure to the supercritical medium. Better protection was attained by suitable coatings, although there were clear differences in the protective capabilities between different coating types, and some challenges remain in applying (and repairing) coatings for the internal surfaces of welded structures. The materials performance seems to be worse in supercritical than in subcritical conditions, and this appears not to be only due to the effect of temperature. The implications are considered from the point of view of the operating conditions and materials selection for future power plants.

Keywords: oxidation, steel, coating, supercritical, power plant

1. Introduction

The operating efficiency of thermal power plants (steam plants) is largely dependent on the applied temperature and pressure before turbine. These are in the current base load plants at most about 600-620°C/300 bar for the supercritical high pressure part of the cycle, and effectively limited by the available materials. One of the life-limiting damage mechanisms for power plant components can be steam side oxidation [1-7]. The ACCEPT (COST 536) project aimed to establish new materials solutions up to the superheating temperature of 650°C. Under such ultrasupercritical (USC) conditions common standard steels are unlikely to perform well, and it is also possible that load-bearing materials need to be protected from the environmental attack by coatings. However, is not clear which kind of alloys or coatings could be best for the purpose, and therefore several candidate materials have been subjected to testing in the COST project. Although supercritical power plants have been operated since 1960's, appropriate laboratory scale testing facilities for high-end supercritical conditions are not common. This work has made use of the VTT USC autoclave that provides circulating supercritical water with controlled conductivity, pH and dissolved oxygen (DO_2) content up to 695°C / 420 bar. The principal objective was to compare the oxidation performance of selected COST 536 materials (ferritic, austenitic and coatings) under the selected reference

conditions of 650°C/300 bar, and to assess the potential applicability of the materials for future ultra-supercritical (USC) power plant.

2. Materials and methods

The selected materials to be tested included four COST base materials, two COST reference materials (P92 and 316LN), and nine coatings on P92 (see Tables 1 and 2). The base material samples were 25 x 15 x 5 mm coupons (Fig 1a) that were flat ground to N7 (Ra = 1.6 μm) on the surfaces, degreased and washed according to the instructions of the COST 536 Oxidation Group before testing. The coated specimens were similar coupons of P92 steel that were coated by the coating providers and then oxidation tested in the as-delivered condition. The coupons were attached to a rack (Fig 1b) with a pin through an insulated hole. The rack with coupons was inserted into the USC autoclave (Fig 2) for oxidation testing.

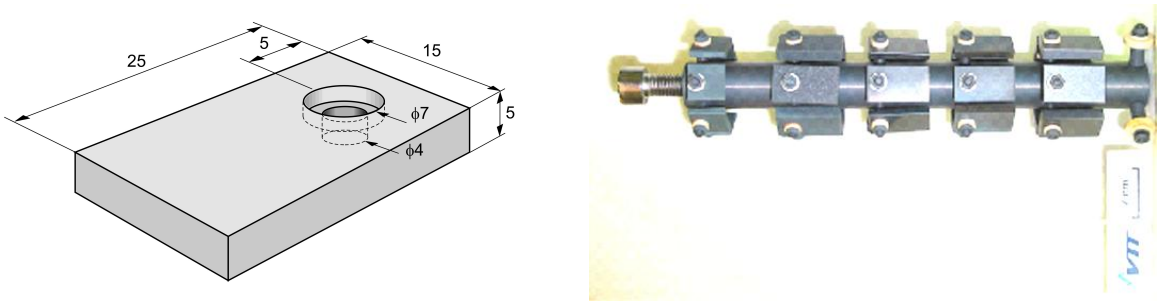
Table 1. Composition of the COST base (bulk) materials [1)]

Mat'l	C	Si	Mn	Cr	Ni	Mo	V	W	Nb	Al	N	B
CT3	0.2	0.3	1.0	10.0	-	1.5	0.2	-	0.06	-	0.02	
CT7	0.2	0.3	1.0	11.5	-	1.5	0.2	-	0.06	-	0.02	
VM12	0.12	0.48	0.37	11.6	0.31	0.28	0.25	1.58	0.044	-	0.078	
P92	0.1	0.3	0.4	9	-	0.45	0.2	1.8	0.06	0.03	0.05	0.003
316LN	0.018	0.22	1.75	16.8	12.2	2.65	-	-	-	-	0.15	-
BGA4	0.11	0.49	6.1	22.9	15.4	0.14	0.31	1.49	0.61	-	0.185	0.007

1) Also 2.7% Cu in BGA4

Table 2. Coatings on P92 for the COST test program

Provider	Type / mark	Notes
MPA Stuttgart	CVD siliconising / MPA Si	Heat treatment by Alstom
INTA	Thermal spray / HVOF	-
INTA	CVD / Si	-
INTA	CVD / Cr	-
Alstom	Aluminising / Al	-
Alstom	HT chromizing / Cr	-
Alstom	Thermal spray / CrC	-
A Univ Thess	Boroaluminising / TES 92	Reduced coupon size
A Univ Thess	Boroaluminising / TES 91	Reduced coupon size



a) b)

Fig 1. a) Coupon for USC oxidation testing; b) test rack for multiple (insulated) coupons

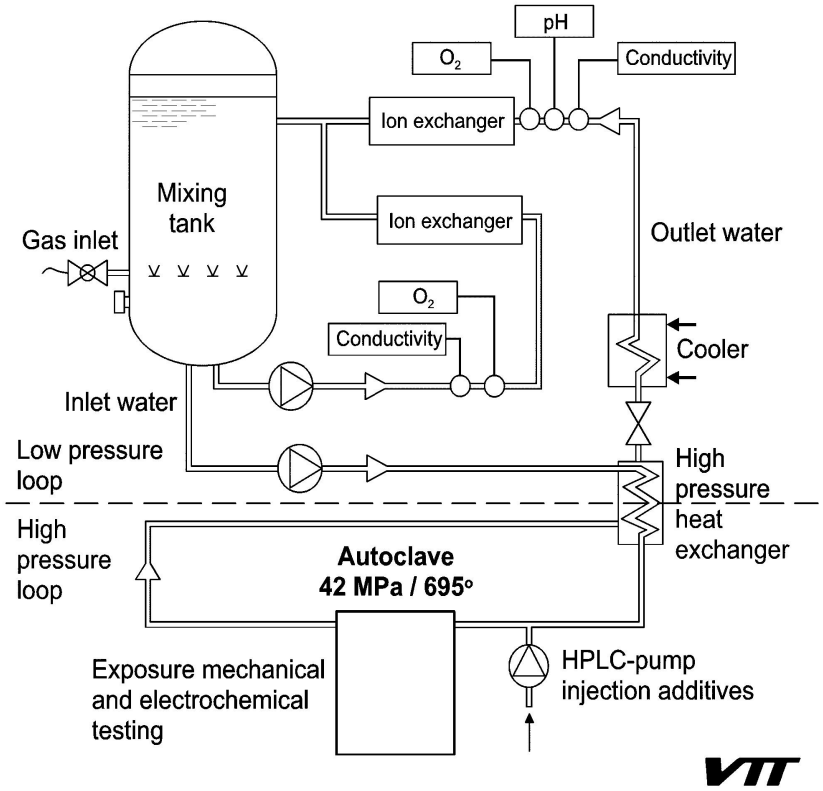


Fig 2. The VTT autoclave system for USC testing

The testing medium was supercritical water at 650°C and 300 bar, controlled to contain 125 ppb dissolved oxygen, pH between 8.0 and 8.5 (target value at 8.4), and conductivity below 0.15 µS/cm. The water chemistry was set in accordance with EN 12952 and VGB guideline for supercritical plant. The flow rate of the medium in the autoclave was set at 5 ml/min.

The testing scheme included three consecutive test runs: first test run with exposure for 24 hours with new coupon samples; second test run for 160 hours with new coupon samples, and third test run for 1340 hours with the same coupon samples (160 h + 1340 h = 1500 h). For each test run, the coupons were checked for mass change and surface layer (oxide) thickness. The layer thickness was obtained by central cross-section microscopy as the mean thickness ± standard deviation of cross-section areas avoiding sample corners (and regions of apparent deviations in e.g. coating preparation).

3. Results

The overall oxidation testing results are summarised in Table 3 for bulk materials and in Table 4 for coatings. The corresponding trends in terms of oxide thickness are shown in Fig 3 for the bulk materials and in Fig 4 for coatings. The indicated oxide thickness is not really a unique measure of the damage, and includes here some influence due to other mechanisms such as surface spalling/wear and internal oxidation. For well known reasons, the indicated mass change is even less unique measure of oxide growth.

Table 3. Oxidation of metallic (bulk) materials after 1500 h at 650°C/300 bar

Material	Δm, mg/cm2	Oxide thickn., μm	Observations / notes
CT3	13.45	91 ± 6	Extensive oxidation
CT7	13.56	90 ± 15	Essentially as CT3
VM12	12.42	83 ± 10	Essentially as CT3
P92	55.69	165 ± 10	Poor oxidation resistance
316LN	8.17	70 ± 25	Not better than CT3, CT7 or VM12
BGA4	0.28 [1)]	2 ± 1	Best (bulk) performance

1) exposure time 1340 h

Table 4. Oxidation of coated materials after 1500 h at 650°C/300 bar [1)]

Coating	Δm, mg/cm2	Oxide thickn., μm	Observations / notes
MPA Si	14.44	140 ± 20	Not protective
INTA HVOF	20.74	~ 50	Thick coating (400 μm)
INTA Si	13.70	150 ± 10	Not protective
INTA Cr	6.83	85 ± 15	Not protective
ALST Al	4.00	(100 ± 50)	Spalling, cracking (~200 μm aluminide)
ALST Cr	0.22	10 ± 5	Best coating performance
ALST CrC	1.99	10 ± 5	Thick coating (~200 μm)
TES 92	(-0,41)	140 ± 10	Partial spalling
TES 91	4.05	75 ± 10	Partial spalling

1) note that here “oxide thickness” = thickness of damaged layer (oxide, lost material etc.)

It is seen that of the bulk materials (Fig 3), most behave rather similarly, except for P92 that is oxidising very fast, and the austenitic alloy BGA4 that shows an excellent oxidation resistance under the tested conditions. Most coatings also appear not to be particularly resistant to oxidation under the tested supercritical conditions, and the best oxidation resistance was shown by the chromium coating prepared by a high temperature diffusion process (Fig 4).

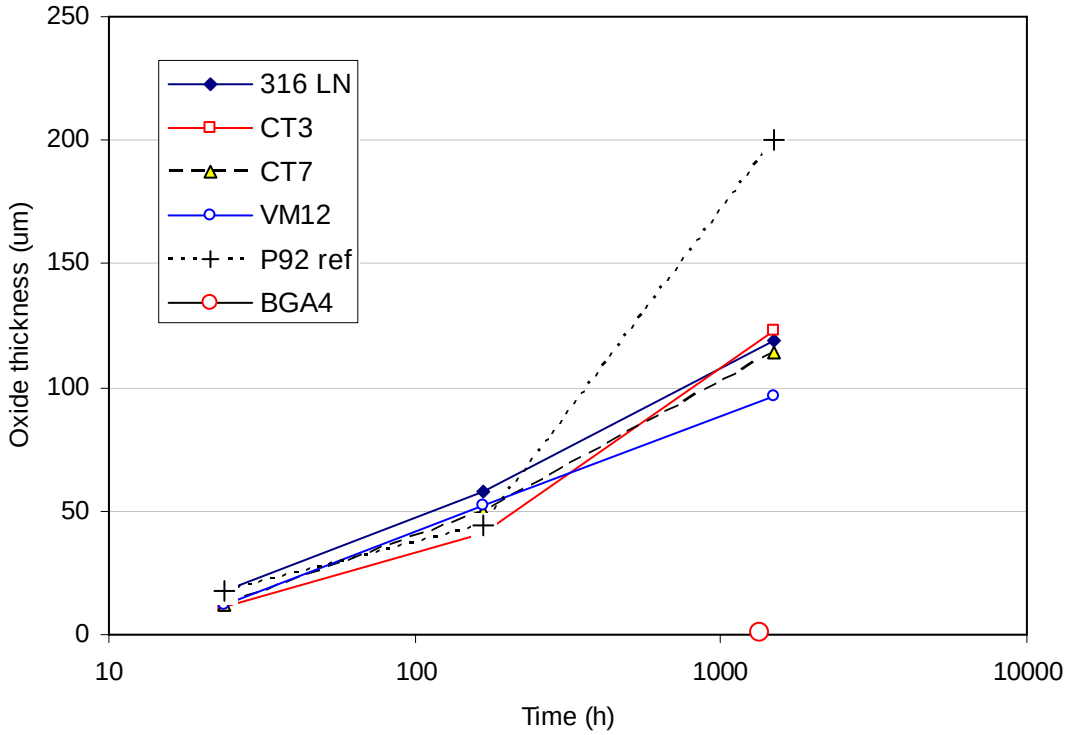


Fig 3. Development of the observed oxide thickness in the metallic (bulk) test materials

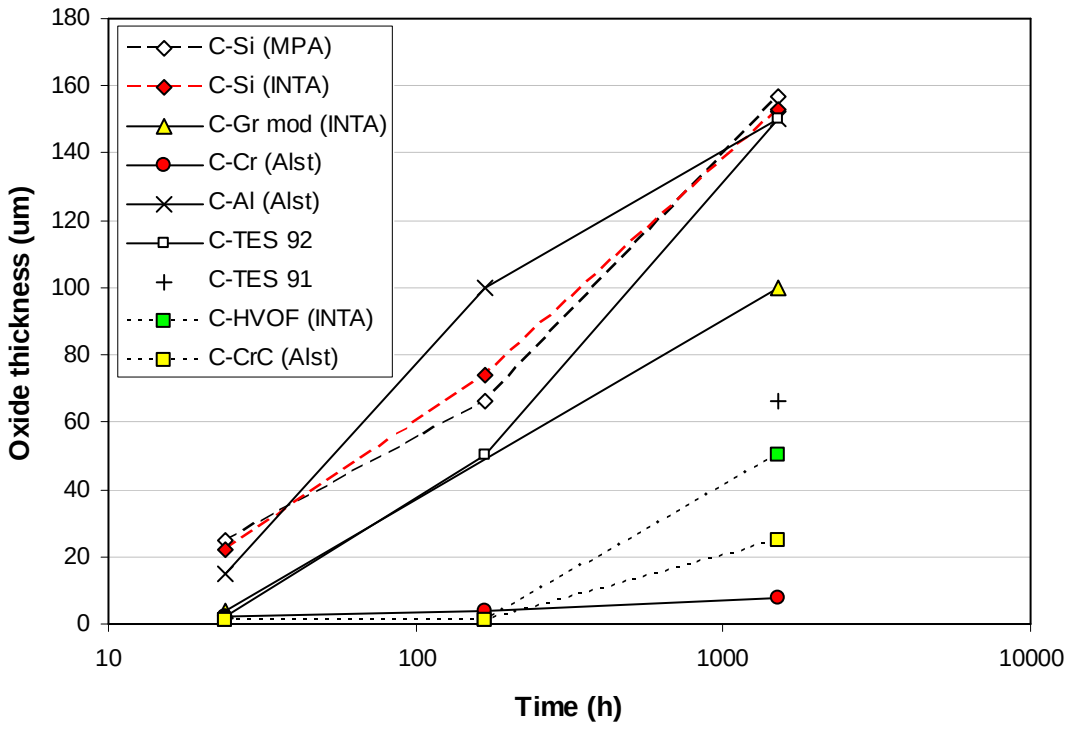


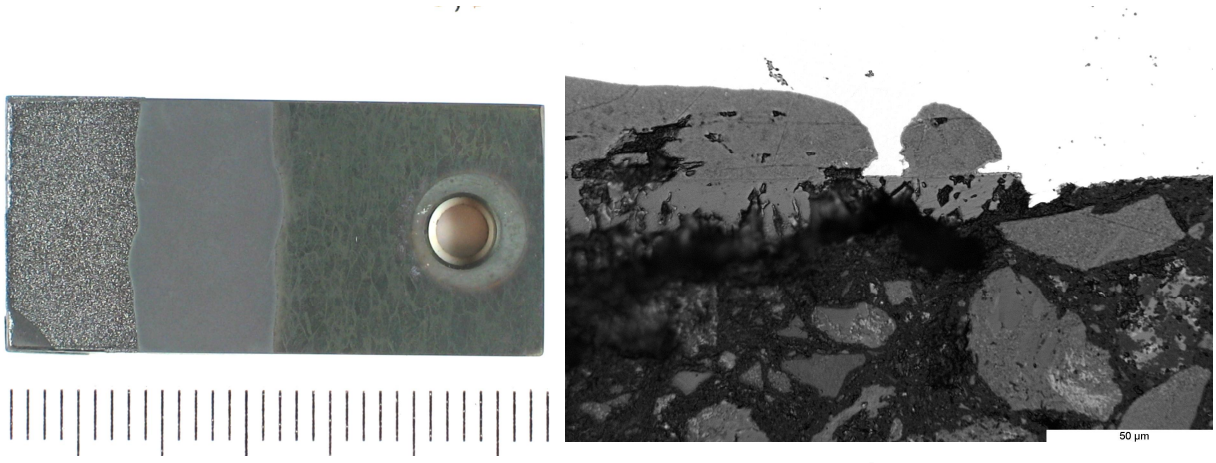
Fig 4. Development of the oxide thickness in the coated coupon samples

4. Discussion

The results show that a fair protection against oxidation at USC conditions (1500 h at 650°C/ 300 bar) was is only obtained for surfaces with a chromium content of more than about 20%. Apparently good performance was provided by the COST (Corus) austenitic steel BGA4 with about 23% Cr. In contrast, the austenitic steel 316LN with 17% Cr was oxidising nearly equally fast as the ferritic COST steels CT3, CT7 and VM12 (10.0-11.6% Cr) which in turn were not very different from each other in terms of oxidation performance. As can be expected, P92 showed poor oxidation resistance at the tested conditions.

Consistent with the results from bulk metal samples, the high temperature chromized coupons performed best of all coatings, although also aluminide coatings could perhaps have reasonable potential in USC service. The tested aluminide coatings were probably either too thin or thick, resulting in perforation or cracking and partial oxidation below the coating. Silicon based coatings appeared not to be resistant to oxidation at the tested supercritical conditions, and possibly are therefore not well suited for USC plant. The autoclave test facility is mainly reserved for short and medium term testing (below about 2000 h), and therefore phenomena that only appear in longer term may not show themselves clearly. In the present work this was usually not a limiting factor, as most materials and coatings were not performing very well under the selected test conditions.

The test program did not include more conventional high-chromium austenitic steels or nickel based alloys as reference materials. Such alloys are considered as candidate base materials for the hottest sections of the future USC plant for the temperature range of about 620-720°C. Fig 5a shows a test coupon after 1000 h at similar testing conditions as above, this time for a weld between a conventional stainless steel type 347 and a nickel alloy, using a nickel-based consumable. The Ni-based parent metal (PM) and weld metal (WM) have performed well under these conditions, while type 347 steel is strongly attacked (Fig 5b). Again, one reason is apparently the relatively modest chromium content of type 347 steel.



a) b)

Fig 5. Coupon with a weld exposed for 1000 h at 650°C/300 bar, 125 ppb DO_2, pH 8.0-8.5; a) cross-section from the left: 347 steel / Ni-based WM / Ni-based PM, b) oxide cross-section at the 347/WM borderline (metallic part up, unetched).

Use of expensive nickel alloys must be minimised in a competitive plant, and the high thermal expansion coefficients of austenitic steels are also not very attractive for thick wall piping, headers or turbine components. Therefore, an incentive remains for the development of (somewhat elusive) higher chromium ferritic steels and improved oxidation resistant coatings that could withstand the aggressive internal environment of the future USC plants at higher temperatures than today. At least in case of coatings, further potential for improvement is very likely.

5. Summary

The test materials including the coated samples have been tested under USC conditions (300 bar / 650°C) for bulk and coated test materials provided by the partners in the Oxidation Group of the COST 536 (ACCESS) project. The materials included reference base materials, experimental COST steels and several different types of coatings on P92 steel. The testing results show differences in the oxidation rates by about two orders of magnitude, and very few materials appear to exhibit satisfactory performance in simulated USC service.

In general, none of the tested bulk ferritic/martensitic steels (CT3, CT7 or VM12) performed well in USC condition, and P92 with about 9%Cr (and 2% W) showed particularly poor resistance to oxidation in USC water. Of the austenitic grades, 316LN that constains 17% Cr was not better that the 10-11.6%Cr ferritic steels. The COST/Corus steel BGA4 with 23% Cr showed best oxidation resistance of all tested bulk materials.

Si coatings were found to be unprotective under the USC testing conditions, while Cr coatings were best, consistently with the experience on bulk steels. Al coatings could also be relatively protective but the tested aluminium based coatings were probably not ideal for the testing program. Further improvement potential is likely particularly for the coatings.

The test program did not include high-chromium austenitic steels or nickel based alloys that are widely considered as candidate materials for future USC plant at the temperature range of about 620-720°C. The good oxidation properties of certain Ni alloys have been demonstrated under USC conditions, also for Ni-based welding consumables. It apparently remains a challenge to develop any type of steels or iron-based alloys that could challenge Ni alloys in this respect. However, any improvement in the performance of steels would be useful to minimise the use of expensive Ni alloys, and the economical incentive also applies to protective coatings. In the present work, high chromium alloys and coatings showed best performance against oxidation, but other compositions such as those applying high Al content could also be considered as potential basis for future improvement.

Acknowledgements

PA, JS, AT and SP acknowledge the financial support by the Finnish Funding Agency for Technology and Innovation, and by the national industrial group in the LC-Power project. AA, MG and RM wish to acknowledge V. Gonzalez for her important contributions to the results as well as the Spanish Ministry of Science and Innovation for financial support (ENE2008-06755-C02-01).

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