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Assessment of the corrosion behaviour of structural materials in the water coolant of ITER

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Abstract

This paper presents the most recent results on the corrosion behaviour of austenitic stainless steel and copper alloys in ITER water coolant conditions, and discusses their relevance to the structural integrity of the in-vessel components. The uniform corrosion of stainless steel (SS) 316L(N)-IG in water is not a limiting factor in ITER. No stress corrosion cracking (SCC) is observed on unirradiated 316L(N)-IG in pure water, water plus hydrogen, and water plus oxygen and/or hydrogen peroxide in the temperature range 90–320°C. No SCC of 316L(N)-IG SS is observed during in-pile constant deformation tests on specimens irradiated at 200°C in water plus oxygen (>10 wppm) and hydrogen peroxide (>3 wppm) up to about 3 dpa. Corrosion tests of copper alloys have been performed in an autoclave with deaerated and demineralised static water. The corrosion rate varies from 0.3 up to 7 μm/y depending on exposure time, temperature and pH. Current requirements for water chemistry are presented in the paper.

1. Introduction

The current design of ITER components and the materials proposed for each of them is presented in [1–3]. High purity deaerated water is specified as the coolant for ITER in-vessel components. Austenitic steel 316L(N)-IG and Cu alloys (CuCrZr-IG and CuAl25-IG) are in contact with water. So environmental effects (such as water) should be taken into account for the assessment of the structural integrity, life time and safety points of the components. The corrosion issue of the materials proposed for the primary water coolant loops under ITER working conditions is the main topic of the R&D results described in this paper.

2. Chemistry and water coolant parameters

The existing experience of fission reactors and the other industrial facilities was taken into account for the specification of the water chemistry for the ITER. The proposed water chemistry is given in Table 1. This specification gives median values and upper limits for action. The median values are defined for the long term reliability. Upper limit is defined for corrective measures within a short time if water parameters will exceed the upper limit. Some of the water parameters are not yet defined precisely. Clarification of these parameters is one of the goal of R&D activity. The pH of the water shall be neutral at room temperature for the proposed parameters. Addition of hydrogen is necessary to suppress radiolysis.

Water coolant parameters of the ITER vacuum vessel (VV) and in-vessel components are given in Table 2. Coolant flow is arranged so that stagnant zones can be excluded. Corrosion of VV materials will be very low and will not impact the life time.

The corrosion behaviour of materials used for the components with higher temperature and coolant rate

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Table 1
Water chemistry specification for vacuum vessel and in vessel components

Parameters of water reactor during operation [a]	Median values	Upper limits for action
Conductivity (at 25°C), μS/cm	<0.1	<0.3
Hydrogen (cm^3/kg at STP/wppm)	$\approx 25/2$	
Hydrogen peroxide (wppb)	<100	
Oxygen (wppb)	<1	<10
Chloride (wppb)	<1	<5
Fluoride (wppb)	<1	<5
Sulphate (wppb)	<2	<5
Copper (wppb)	<2 [b]	<5 [b]
Iron (wppb)		<5 [b]
Hardness (Ca, Mg, etc.)(wppb)		<5 [b]
Total organic (wppb)		<100 [b]

[a] ECP (mV SHE) parameter indicating the SS state should be defined during post EDA.
[b] Recently specified parameters that should be confirmed during R&D.
pH shall be neutral at room temperature.

Table 2
Water coolant parameters of the vacuum vessel and in-vessel components

	Vacuum vessel	Back plate	Primary wall, module	Baffle	Limiter	Divertor
Inlet temperature, °C	100	140	140	140	140	140
Outlet temperature, °C	109	192 max	192 max	192 max	181 max	174 max
Pressure, MPa	1–2	3.8	3.8	3.8	3.8	3.8
Pressure drop, MPa	~0.1	~0.1	0.4–0.5	0.5–0.6	0.8–1.0	~1.5
Coolant velocity, m/s	0.001–0.005	5	2.5–5.5	3–4	7–9	10–12 max [a]
Materials	316L(N)-IG and SS 430, 30467 inserts	316L(N)-IG	316L(N)-IG tubes	CuA125-IG with 316L(N)-IG inner tube	CuA125-IG and 316L(N)-IG SS	CuCrZr-IG, CuA125-IG, 316L type SS (cassette body)

[a] In high heat flux area.

are the most critical ones and will be considered in this paper.

3. Corrosion behaviour of stainless steel

3.1. Uniform corrosion

The uniform corrosion of 316 type SS in a water environment is well known and is not a limiting factor in ITER, as can be inferred by the extensive experience on the use of austenitic SS in light water reactors. Appropriate water chemistry has to be provided to maintain acceptable levels of uniform corrosion and to avoid appreciable mass transfer or local corrosion damage.

Available data on the corrosion rate in temperature range 134–200°C are presented in Fig. 1. Different fitted equations are proposed in [4–6] (see Fig. 1). These variations are explained by the different test temperatures and type of test. Some tests have been performed on the standard specimens installed in the reactors circuit, others by measuring of the corrosion rate in the autoclave. Measurements were performed on the austenitic steel 321 type. One may assume that uniform corrosion rate of austenitic steel 316L(N)-IG should be similar to the 321 type. Water chemistry in all experiments was close to that one specified for the ITER.

Summarising available experimental data (from this study and published ones) the following equation can be proposed for the estimation of average corrosion rate of austenitic SS in temperature range 150–200°C: $\log K = a + b \log \tau$, where K is corrosion rate in g/(m^2 h), τ-exposure time in h, $a = -1.77$, $b = -0.548$. Depending on temperature **a** may vary from -2 to -0.88 [6].

It should be concluded that uniform corrosion is not a critical issue for the structural integrity and life time of the ITER components. But the precise estimates of corrosion rate is required for the assessment of corrosion products activation.

3.2. Stress corrosion cracking

316L(N)-IG steel with the proposed composition is not prone to SCC in the specified working conditions.

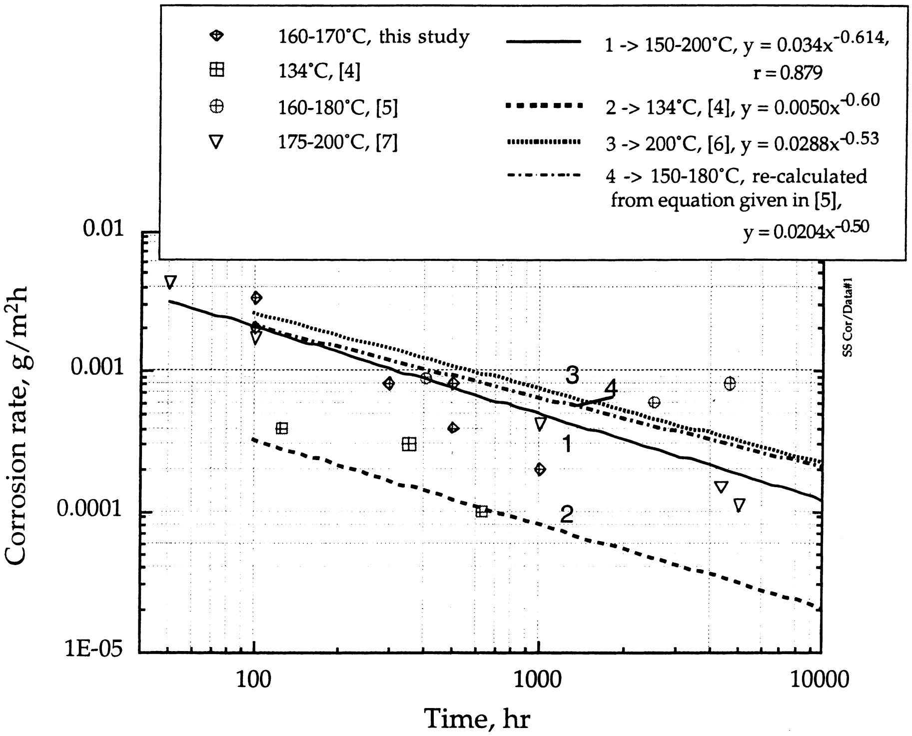

Fig. 1. Corrosion rate of austenitic steels in temperature range 134–200°C. Deaerated, demineralised, neutral pH water. Correlation coefficient *r* is given only for the fitted equation of experimental data in temperature range 150–200°C.

On the basis of existing experience and tests results, austenitic steel might have SCC at temperatures <200°C if chlorine content exceeds ~2 wppm in aerated neutral water [7]. Specified level of chlorine in the water for the water chemistry correction during short period of time (action of operational staff, see Table 1) is 5 wppb that is orders of magnitude lower that will results in the appearance of SCC.

Additional heat treatments during components manufacturing (2–4 HIP cycles [2]) result in minor structure changes, in particular grain growth (from grain number variation 5–6 to 2–6 according ASTM E112), decrease of strength (within the minimum specified values), increase of ductility and additional ferrite formation and precipitation (up to 8% of ferrite). These structural changes are due to HIPing for 2–4 h at 1050–1100°C, plus 2–4 h at 940°C, plus 2–4 h at 850 and cooling of the components in the HIP facility furnace. But these changes of structure should not result in susceptibility of steel to the SCC. Susceptibility to SCC due to carbide precipitation is not a concern for the ITER steel grade. The exposure more than 100 h at the temperature 650–700°C may give a susceptibility to SCC of this steel grade [8].

Irradiation-assisted stress corrosion cracking (IASCC) is a concern for high dose irradiation at high temperatures. Irradiation courses the re-distribution of alloying elements near the grain boundary. Theoretical calculations performed by Simonen et al. [9] show that radiation-induced changes in grain boundary chemistry decrease with decreasing temperature and exposure time. This was one of the reasons for specification a low temperature of the coolant in ITER.

Post irradiation SCC experiments performed by Bell et al. on 316 SS, irradiated and tested at 60, 200 (8 dpa, He/dpa = 15 appm), showed that under slow-rate tensile testing transgranular failure with uniform elongation (>10%) and total elongation of 27% and 13% was observed at 60°C and 200°C, respectively [10]. Intergranular SCC was observed only for higher temperatures of irradiation (at 330°C and 400°C).

The results of R&D performed on the 316L(N)-IG SS indicate the following [11]:

1. There was no SCC of unirradiated 316L(N)-IG observed with Slow Strain Rate Testing (SSRT) and Constant Deformation Testing (CDT) in pure water, water plus hydrogen (up to 2 wppm), and water plus oxygen (~0.3 wppm) and/or hydrogen peroxide (1–10 wppm) in the temperature range 90–320°C.
2. There was no SCC observed with in-pile testing using Constant Deformation Test specimens irradiated at 200°C in water plus oxygen (>10 wppm)

and hydrogen peroxide (>3 wppm) up to about 3 dpa.

3. There was no SCC of unirradiated SS at 320°C with SSRT and CDT in neutral solution of chloride, sulphate and copper ions, containing about 2 wppm of hydrogen. However, with addition of 1–30 wppm of hydrogen peroxide to simulate possible water radiolysis, SCC occurred on sensitised specimens after 1500 h of exposure.
4. There was no corrosion fatigue cracking of 316L(N)-IG SS at 320°C after 10^5 cycles at 0.5% strain amplitude.

Investigations performed by Chopra, Kassner et al. [12,13] showed that SCC was observed at temperatures >150°C under crevice conditions in water containing ~7 wppm of O_2, ~6 wppm of H_2O_2 and 0.1 wppm of SO_4^{2-}. Chloride concentration should be more than 60 wppb to have SCC at the crevice-weldment specimens and temperature ~200°C. No SCC was observed during SSRT tests of crevice-weldment specimens in oxygenated water containing 60 wppb of chloride.

It is possible to conclude on the basis of existing data there will be no SCC effects on the 316L(N)-IG SS under the normal operation conditions (in the specified water chemistry) in the unirradiated state. Irradiation during Basic Performance Phase (BPP) of ITER to doses up to 3 dpa should not results in IASCC cracking.

Nevertheless, SCC may take place in the crevice condition and if chloride concentration will exceed 60 wppb. Specification of the limit, where SCC may occur in the crevice region is the main goal of future R&D.

3.3. *Galvanic corrosion effect*

On the basis of galvanic current measurements [14], Galvanic Corrosion between Cu-based alloys and 316L(N)-IG SS is minimised by maintaining very high water purity. Adding hydrogen inhibits the galvanic corrosion at high temperature, but has little effect at low temperature. In high purity deaerated water the potential difference and hence the galvanic current between SS and Cu alloy is small (<1 μA/cm^2). Copper alloy is more noble compared to SS and is not corroded. Galvanic corrosion should be on the SS part, and the value is very small in the ITER working conditions.

4. Corrosion of Cu alloys

4.1. *Uniform corrosion*

Copper is noble relative to hydrogen and its dissolution in a water not containing oxygen should not occur. But in reality even a very small oxygen content in the water results in oxide layer Cu_2O formation. Growth of this oxide leads to formation of the CuO and $Cu(OH)_2$ porous layer at the surface that results in increase of Cu release to the water. Oxygen content in the water is one of the most critical factors affecting the corrosion and the corrosion product release to the water. Water velocity and pH are the important parameters affecting on the corrosion behaviour of Cu alloys. Available data showed that corrosion rate and corrosion product release to the water decreases with increase of pH from 5 to 9, and is minimum at pH ≅ 8–9 [15]. It was also pointed out that corrosion varies with factor of 15 with flow velocity changes from 0 to 4 m/s [16]. The dominating factor on the flowing water is the oxygen content in the water and pH.

Investigation of uniform corrosion of CuCrZr have been performed in autoclave with deaerated and demineralised static water with pH = 7 and oxygen content <25 μg/kg at the temperature 100°C and 180°C and with pH = 8.5 that was achieved by the addition of KOH in the water. Test duration was up to 3000 h. Results of investigation are presented in Fig. 2. The fitted equation and correlation coefficient are also given in the figure. The experimental data show that increase of temperature from 100°C to 180°C results in increase of corrosion rate about five times. Corrosion rate is decreased with increasing pH from 7.0 to 8.5 only during the first ~1000 h; for a long term exposure corrosion rate becomes higher than that of the neutral pH. Corrosion rate also depends on the type of alloy. This was demonstrated in Fig. 2, where corrosion rate of CuNiCrSi alloy are given for comparison.

Additional data on the corrosion measurement of proposed for ITER Cu alloys (CuCrZr and Glidcop CuAl25) in different water conditions and type of tests are presented in Table 3. The data shows that corrosion rate may vary by a factor of ~20 depending on the water chemistry and test conditions. Water flow results in increase of corrosion rate due to getting wash of the CuO layer from the surface. Actually it cannot be called as corrosion–erosion effect because of dense Cu_2O layer remains at the surface, and most probably this phenomena was due to washing and formation of the porous CuO at the surface of dense Cu_2O. A possible mechanism of corrosion of Cu–Ni alloys was proposed in Ref. [17]. Initially formed Cu_2O layer transforms with the time to the CuO and NiO that are easily released to the water.

4.2. *Localised corrosion effect*

Localised corrosion (cracking), pitting of copper can take place if the pH of water is low. High concentration of chlorides (>0.1 M) and low pH is necessary to get the localised corrosion significant [14]. Pitting was not revealed during existing experiments. Water chemistry specified for ITER should not give a localised or pitting corrosion effect.

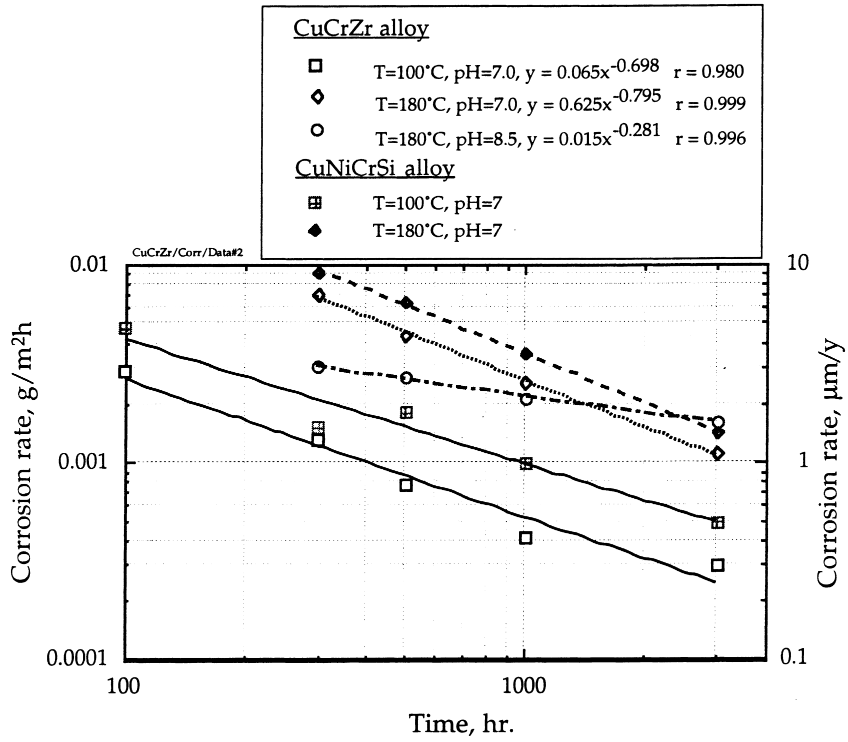

Fig. 2. Measured value of corrosion rate of the CuCrZr and CuNiCrSi alloys.

Table 3
Results of corrosion measurements of copper alloys proposed for the ITER

Material	Test conditions	Corrosion rate μm/y	Method of measurement	Reference
CuCrZr	Deaerated and demineralised static water. Oxygen <25 μg/kg, pH = 7.0. Test temperature ~100°C. Test duration – up to 3000 h	0.3–3	Weight changes	
CuCrZr	Deaerated and demineralised static water. Oxygen <25 μg/kg, pH = 7.0. Test temperature ~180°C. Test duration – up to 3000 h	1–7	Weight changes	
CuCrZr	Deaerated and demineralised static water. Oxygen <25 μg/kg, pH = 8.5. Test temperature ~180°C. Test duration – up to 3000 h	1.5–3	Weight changes	
CuA125	Water flow – 10 m/s, 10^{-5} M H_2O_2. Temperature – 95°C. Test duration – 1000 h (Flow is parallel to the surface)	31	Weight changes	[18]
CuA125	Water flow – 10 m/s, 10^{-3} M H_2. Temperature – 95°C. Test duration – 1000 h (Flow is parallel to the surface)	17	Weight changes	[18]
CuCrZr	Water flow – 10 m/s, 10^{-3} M H_2. Temperature – 95°C	~10	LPR technique	[18]
CuA125	Water flow – 0 m/s, 10^{-3} M NaOH,pH = 11.0	14	Tafel extrapolation technique	[18]
CuA125	Water flow – 9.3 m/s, 10^{-3} M NaOH, pH = 11.0	89	Tafel extrapolation technique	[18]
CuA125	Water flow – 0 m/s, 10^{-3} M $NaHCO_3$, pH = 8.0	7	Tafel extrapolation technique	[18]
CuA125	Water flow – 93 m/s, 10^{-3} M $NaHCO_3$, pH = 8.0	80	Tafel extrapolation technique	[18]

The investigation of possible crevice effect was studied on the mechanically attached CuCrZr and SS plated in the autoclave with water conditions described above. The result of tests during 2000 h both in neutral water and in the water with pH = 8.5 shows that corrosion of Cu alloy even decreases in such conditions. It could be explained by the galvanic effect (Cu plate was a cathode in this condition) and by the decreasing of oxygen content in the static water of crevice. It should be pointed out that SS was an anode in such conditions, but there was no increase of corrosion of SS. Most probably this is because of very low level corrosion of SS (below the sensitivity of measurement) and that the difference in potential between Cu and steel is very small, and the galvanic effect in not manifested.

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