**Fusion
Engineering
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Erosion–corrosion tests on ITER copper alloys in high temperature water circuit with incident heat flux

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Abstract

To investigate the erosion–corrosion behavior of the Cu-alloys, i.e. CuCrZr and CuAl25-candidate materials for the manufacture of the diverter cooling channels for ITER, a test loop has been developed for testing erosion–corrosion behavior under high heat flux conditions. The heat loads on the test specimen surface amounts to 10 MW/m^2. Under adverse testing conditions in oxidizing water (5–10 ppm H$_2$O$_2$) at 100 °C, with a flow velocity of 10 m/s and intermittent heat loading, followed by cooling cycles under oxidizing conditions maintained, CuCrZr alloy has shown the formation of a thick surface oxide films (essentially cupric oxide, CuO). This surface layer seems loosely adhesive, and detachable by mechanical or thermal shocks, or by fluid flow velocity effects. Indicated with a rough morphology, surface attacks were somewhat observed in areas after the surface oxide layer spalled off. Present results suggest the necessity for, such as, strict hydrogen water chemistry (HWC), in order to limit the copper corrosion rate or at least the release of copper into the cooling water circuit.
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1. Introduction

Considered as candidate materials for the manufacture of the divertor cooling channels (heat sink materials) in international thermonuclear experimental reactor (ITER) design, some copper alloys have been tested with respect to their erosion–corrosion resistance in high temperature water

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environment under different water chemistries, which is one of the crucial technical issues for the application.

Copper alloys used in fossil plant experience corrosion by several mechanisms. General corrosion is typically of greatest concern, and copper release associated with erosion–corrosion also may be significant in case of high water velocities.

Corrosion behavior of copper alloys strongly depends on the water chemistry [1,2]. It is generally accepted that water oxidation–reduction or redox potentials, so-called ORP, and/or together with the electrochemical corrosion potential (ECP)

of the copper metal, are the key parameters controlling corrosion of copper alloys. These parameters reflect the presence and concentrations of oxidizing impurities (i.e. oxygen) and determine the type of surface oxide formed on the copper alloys.

In high-purity water environments, copper forms two common oxides, i.e. Cu_2O (cuprous oxide) and CuO (cupric oxide), and one common hydroxide, $Cu(OH)_2$. The oxide formation process initiates with the oxidation of metallic copper to cuprous oxide, and cuprous oxide may then be further oxidized to cupric oxide. Under sufficiently reducing conditions, i.e. in water containing low oxygen concentrations, maybe in combination with an oxygen scavenger or reducing agent, the oxide layer on the copper surface consists mainly of Cu_2O. When oxygen concentrations are high enough, both Cu_2O and CuO will form. Differences in this surface oxide (i.e. Cu_2O or CuO, or mixed oxides) are believed to control the ultimate corrosion behavior of the alloy. Many studies have indicated that Cu_2O is the more protective oxide for copper alloy component surfaces. It is widely accepted that the use of low-oxygen levels reduces corrosion [in which case the conditions will favor the formation of Cu_2O on the copper surface (as opposed to CuO)] [3]. Most published laboratory investigations and field research data demonstrate enhanced metal release rates of brasses and copper-nickel alloys as oxygen concentration increases from < 30 to 100–500 ppb [2]. Obviously, oxygen is one of the most critical factors affecting the corrosion and the corrosion product release into the water. Thus, the presence of oxidizing species in ITER reactor, such as water radiolysis yield of H_2O_2 and oxygen, will be of a great concern regarding the corrosion performance of copper alloys.

On the other hand, a concomitant increase in the amount of porosity facilitates the mechanical disruption and release of CuO into the water. Therefore, the total metal loss from the structural surface of Cu or Cu alloys may be caused not only by (electrochemical) reactions, but also by physical degradation (wear) of the surface-erosion corrosion. Regarding erosion corrosion, water velocity, particularly at higher speeds, is an important

factor affecting the corrosion behavior of copper and its alloys. Available data show that corrosion may vary by a factor of 15 where the flow velocity changes from 0 to 4 m/s, and velocity effects seemed more pronounce in aerated water then in deaerated water [4]. However, those velocities examined are much lower than that to be expected in the ITER design.

It should also be mentioned here that, in power plants, metals transport activity is higher during start-up and immediately after start-up than during periods of sustained operation. For example, Smith [5], in presenting findings of a copper transport study for evaluating copper deposition in high-pressure heaters, noted that iron and copper levels increased at start-up and remained high for several days thereafter. Hagewood et al. [6] noticed that significant copper corrosion took place during unit shutdowns and start-ups. However, effect of peaking or cycling service on copper corrosion rates has not been considered yet in any ITER task.

A preliminary study of the erosion–corrosion behavior of these Cu-based alloys was already carried out in the early projects NET NWC 2-4 and ITER Task T10 [7]. This paper reports the later study on the erosion–corrosion of the copper alloys in elevated-temperature water in the ITER T-222 (erosion–corrosion testing of Cu-alloys with incident heat flux). Two commercial copper alloys, i.e. dispersion-strengthened alloy (CuAl25), and age hardenable CuCrZr alloy have been proposed for testing.

Suggested for the ITER primary circuit, the testing water parameters are:

– Low conductivity (< 0.1 $\mu\Omega$m/cm at 25 °C),
– Low oxygen (< 1 wppb),
– Contamination levels for chloride and fluoride < 1 wppb

Hydrogen addition is proposed (up to ~ 2 ppm) to suppress the effect of water radiolysis under irradiation, and water velocities proposed for testing are 10–15 m/s.

As part of ITER technology task T-222, a highly sophisticated experimental set-up has been designed and constructed for the evaluation of

erosion–corrosion phenomena under very high heat flux conditions, e.g. the concomitant risk of local boiling phenomena at the copper wall surfaces. Specified heat loads on the test specimen surface amount to 10 MW/m^2, with water velocities up to ~ 10 m/s. The test loop is capable of running under different permanently monitored and controlled water chemistries at elevated temperature and pressure. This experimental set-up allows carrying out an ultimate (erosion–corrosion) test on the feasibility of using the current ITER reference material—CuCrZr alloy—for the envisaged service.

2. Experimental

2.1. Test loop

The high-temperature high-pressure loop described in the previous work [8,9] was modified further to perform erosion corrosion tests with high incident heat flux.

The erosion–corrosion test loop is a completely closed system, and its structure is schematically shown in Fig. 1 [8,9]. This loop is generally divided into two sections, i.e. the conditioning section and the testing section, which are indicated respectively by 'I' and 'II' in Fig. 1.

Important technical function of the conditioning section is to keep the water chemistry during the loop operation, except heating up the loop, building up the pressure, and maintaining the temperature and the pressure. The reservoir used to control the required water chemistry is at room temperature, and different electrodes were plugged into the reservoir to monitor a series of chemical parameters, e.g. redox potential, pH, dissolved O_2, H_2O_2 and H_2 concentrations, and conductivity.

A thermal hydraulic test rig is built in the testing section. Dedicated mock-ups (test sample arrangement—see Section 2.3) were installed inside a high-performance ohmic resistance heating device (Section 2.2), with all necessary safety equipment and auxiliaries [10]. High capacity pump generates a water circulation at the maximum linear flow velocity of 15 m/s through the gauge section of the sample tested.

A picture of the total assembled test loop system is shown in Fig. 2.

2.2. Thermal hydraulic test rig—Ohmic heating device

The thermal hydraulic test rig, i.e. the Ohmic heating device or heat flux test section, used in the present erosion–corrosion test was designed and manufactured by the EFREMOV Institute, Rus-

S: Test section
P1: High pressure pump
P2: High-temp-pressure pump
H: Pre-heater
A: Autoclave with an oven
C: Cooler

V1, V2, V3: 2-way valve
V4: 3-way valve
V5: Pressure valve
T: Tank
G1, G2, G3: Gas bottle
Pot: Potentiostat
Com.: Computer
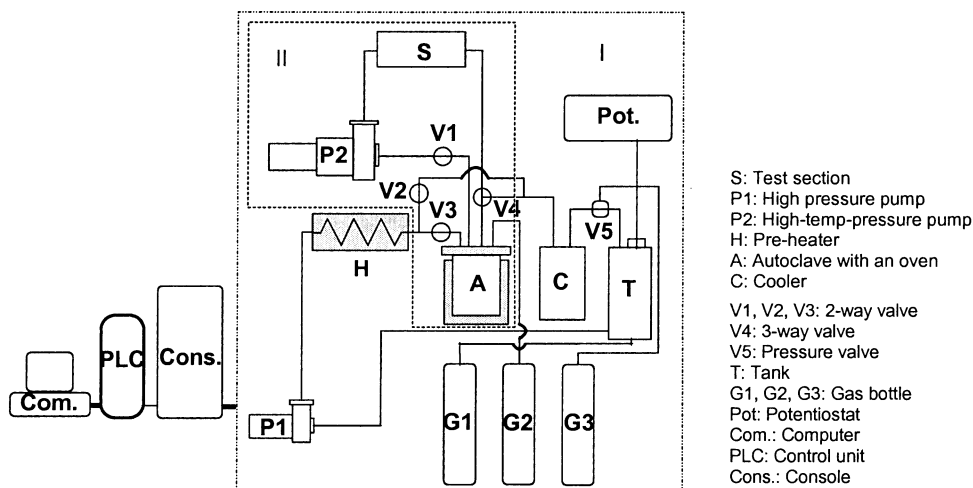PLC: Control unit
Cons.: Console

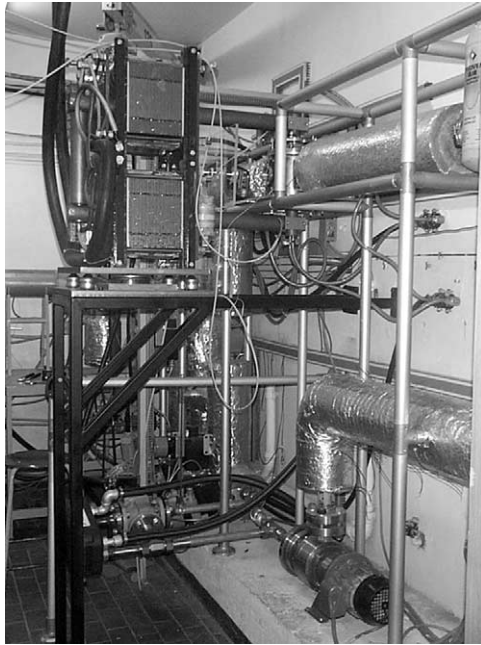Fig. 1. Schematic diagram of high temperature loop for erosion–corrosion tests.

Fig. 2. High-temperature high-pressure erosion–corrosion test loop with incident heat flux facilities.

Fig. 3. Thermal hydraulic test rig—heat flux test section.

sia. It is the main component for investigating the erosion–corrosion behavior of copper alloys with incident heat flux. This test rig allows creating heat fluxes up to 10–12 MW/m² to the mock-ups. An overall view of the heat flux test section is shown in Fig. 3. The different components are schematically represented in Fig. 4.

At the core of this heating device is a graphite insert between the copper mock-ups (see (1) in Fig. 4). This serves as an ohmic resistance heating–element. Heat generated in the graphite insert produces the thermal load on the copper blocks (2) surrounding the tube samples (cf. Section 2.3). The latter are actively cooled by water and are electrically insulated from the rest of the test loop circuit.

The current reaches the graphite heating-element via the mock-up, which is used as contacting electrode. The power supply to the mock-ups passes the high current electrodes (3) with specially designed clamps to ensure a good electric contact between the mock-ups and the high current electrodes. These clamps (4 in total) are used to adjust the compression at each corner of the graphite plate to ensure uniform current distribution and heat fluxes.

A hermetic chamber with glass viewing windows surrounds the whole assembly (4); see also Fig. 3. This chamber is constantly purged with a flow of Argon gas (5) to protect the heat-emission area (i.e. the graphite) from atmospheric oxidation.

2.3. Test specimens

In the present experiment, the pair of mock-ups is made of Alloy CuCrZr, supplied by ENEA, Italy. The construction of the mock-up is such that two cylindrical (tube) specimens were in parallel, and each tube was plugged into a piece of copper metal shaped rectangularly (see Fig. 5). At the inside of each tube is a helicoidal, screw-like insert to stimulate turbulence within the tube. The graphite heating-element was inserted in between the two copper blocks for heat generation.
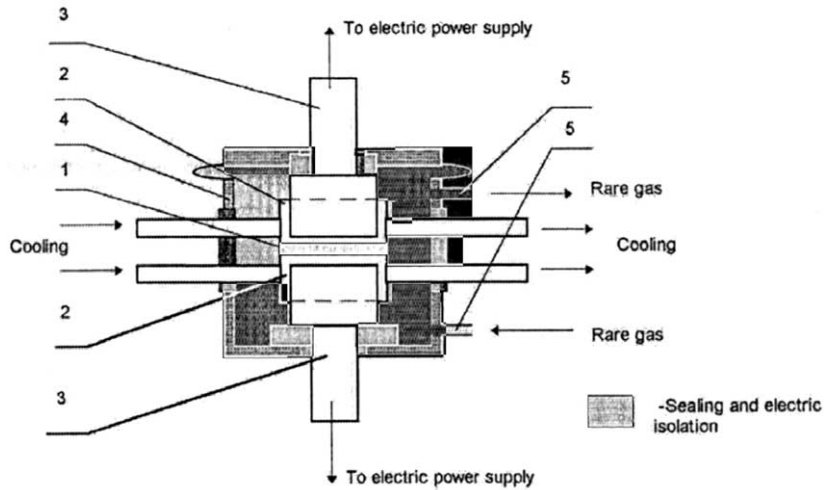
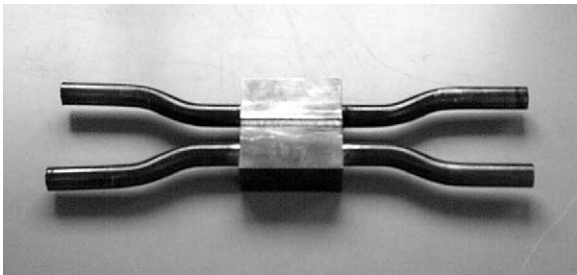Fig. 4. Schematic representation of ohmic heating device.

Fig. 5. Mock-ups used for erosion–corrosion tests with incident heat flux.

2.4. Erosion–corrosion testing

It is clear from the results in Section 2 that the most critical condition is the erosion–corrosion performance of the copper alloys in the presence of H_2O_2. Hence the current tests with incident heat flux are limited to water with H_2O_2 addition.

H_2O_2 is added at regular intervals, to maintain a (high) concentration between 5 and 10 ppm. The feedwater of the loop is continuously purged with nitrogen, but the continuous decomposition of H_2O_2 sets up an oxygen concentration at the inlet of the test section which is typical between 300 ppb and ~ 1 ppm. The redox potential of the water under these conditions is normally around $+200$ mV versus Ag/AgCl (typical values between $+175$ and $+225$ mV, with some extremes to $\sim +230$
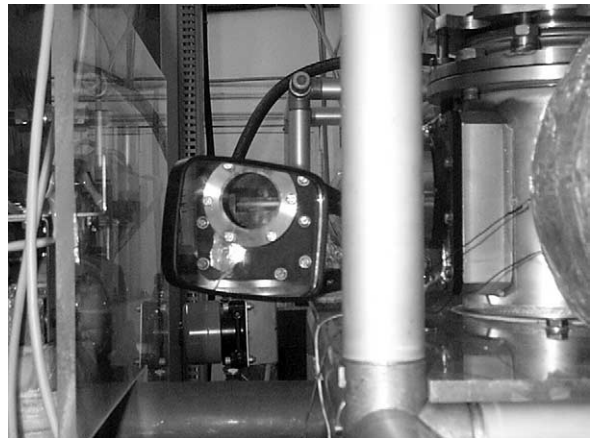

Fig. 6. The graphite heater burning under the heat load.

mV), strongly depending on the dissolved oxygen level.

During heating, the average actual heat load on the specimens was 9.8 MW/m^2. Fig. 6 shows the graphite heater burning under the heat load. However, in some preliminary tests, the lifetime of the graphite heating-element was limited to some 10–24 h. This necessitated regular replacement of the heating element, and the performance of the erosion–corrosion experiment with intermittent heat loads during different cycles.

In actual service, the experiment was typically run for 10–15 h with incident heat flux (9.8 MW/m^2) and a water temperature at the inlet of the test section of 100 °C, followed by a period of $\sim$10 h without heat input and a gradual cooling-down of the test fluid to room temperature. During the replacement of the graphite heating-element, typically the copper sample was only exposed to a stagnant water regime during some 4–5 h. So, a typical cycle is: 10–15 h heat load and high water flow velocity (10 m/s) at temperature (100^+ °C), 5–10 h cooling down to 25 °C at high water velocity, 4 h at zero water velocity (stagnant conditions) and 25 °C. The total duration of the actual experiment with exposure of the sample to the oxidizing water environment amounted to 172 h, with a total of 70 h of heat load on the specimens.

It should also be mentioned that the total heat input into the specimen is not always uniform, probably sometimes leading to local boiling phenomena at the copper alloy wall surface, which may affect the final test outcome. On the other hand, although measures are taken to preserve the nominal water chemistry during the replacement of the graphite heating-element (and the interruption of the heat input), transient conditions (both temperature transients and redox potential—ORP—excursions of the water) cannot be fully avoided with such an operating regime. However, all this should give us a somewhat adverse, at least conservative, view on the potential corrosion performance of the alloy. Nevertheless, on the other hand, these test conditions may also more closely reflect the actual service conditions to which the alloy may ultimately be subjected in the ITER test reactor.

3. Results and discussion

The mock-ups were dismantled right after testing for corrosion inspection. To prepare samples for the evaluation, each mock-up was cut apart along its longitudinal direction, through the central horizontal plane. One part is the half directly attached to the graphite heating-element, and the other half was connected to the high current electrode.

The inner tubing surfaces of the mock-ups were first inspected visually, and then examined using stereomicroscopy and scanning electron microscopy (SEM). The chemical composition of the exposed copper surface and the oxide layer above were further determined with energy dispersive X-ray (EDX) analysis.

3.1. Visual inspection and stereomicroscopy

Fig. 7 shows the inner tube surfaces of the mock-up tested. The upper picture is the inner surface on the side of the mock-up contacting the graphite heating-element, and the lower one is the opposite side.

It was found that a layer of black oxides covered mostly the inner tube surface (see those dark areas in the photographs of Fig. 7). Some areas showed bright under the microscope (see the light areas in Fig. 7), indicating that the oxide layer was already spalled off. This observation suggests that during the exposure period, the copper surface has significantly been oxidized in water containing H_2O_2. The two inclining stripes visible on the inner tube surface indicate the location where the spiral plug was positioned. At some locations,
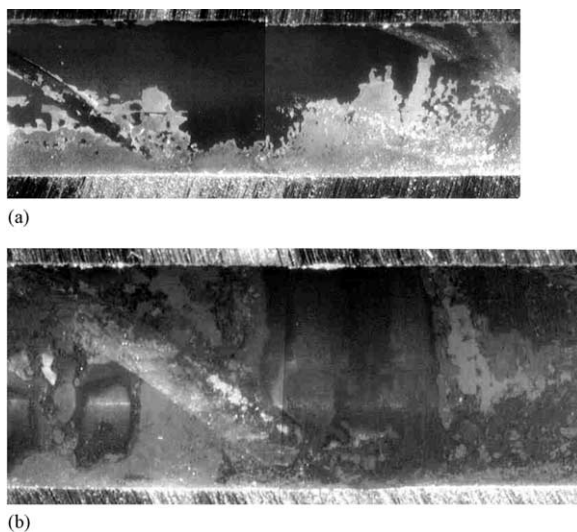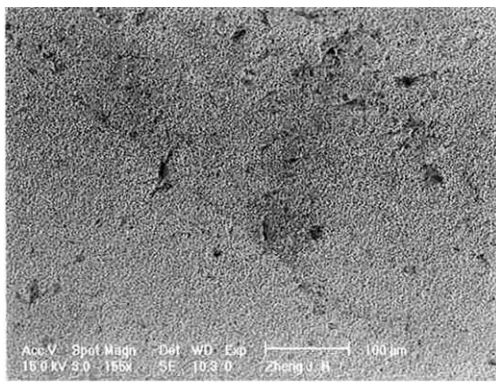

(a)

(b)

Fig. 7. The inner surface of the mock-up tested.

streaming of the water through the narrow gap between the spiral and the tube wall has removed the thick surface oxide layer. However, no clear signs of further erosion corrosion damage were obvious.
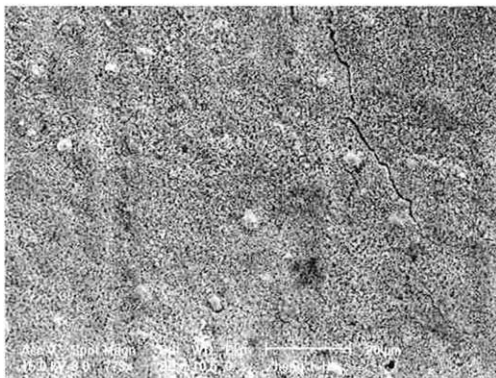
It is believed that spalling off of the oxide layer was due partially to the impact from the high velocity water stream and probably also to the vibration introduced by cutting while sampling. It suggests anyway that the oxide layer is only loosely adhesive to the copper tube surface.

3.2. SEM and EDX

As mentioned previously, a layer of black oxides largely covered the inner surface of the mock-up. Typical morphology of this oxide layer is shown in the pictures of Fig. 8. The morphology of the oxide
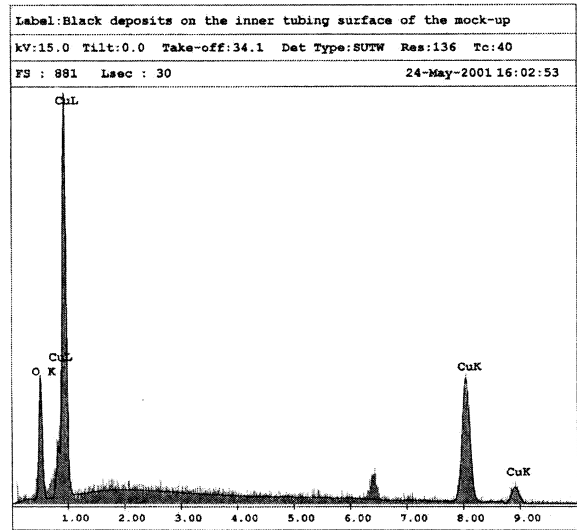

Fig. 9. Typical EDX spectrum of the black oxide layer on the inner surface of the mock-up tested.

layer looks homogeneous. However, some defects (see picture 8a) and cracks (see picture 8b) were often found in the layer.

EDX analysis was carried out on the oxide layer to determine its chemical composition. A typical spectrum of the oxides is shown in Fig. 9, indicating that the black surface layer is indeed essentially consisting of copper oxides. In view of its color, this should essentially be cupric oxide (CuO).

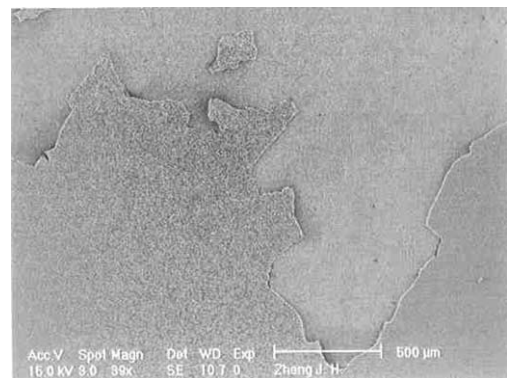Picture in Fig. 10 show the inner surface areas of the mock-ups at places where the oxides were

(a)

(b)

Fig. 8. Typical morphology of the oxide layer on the inner surface of the mock up.

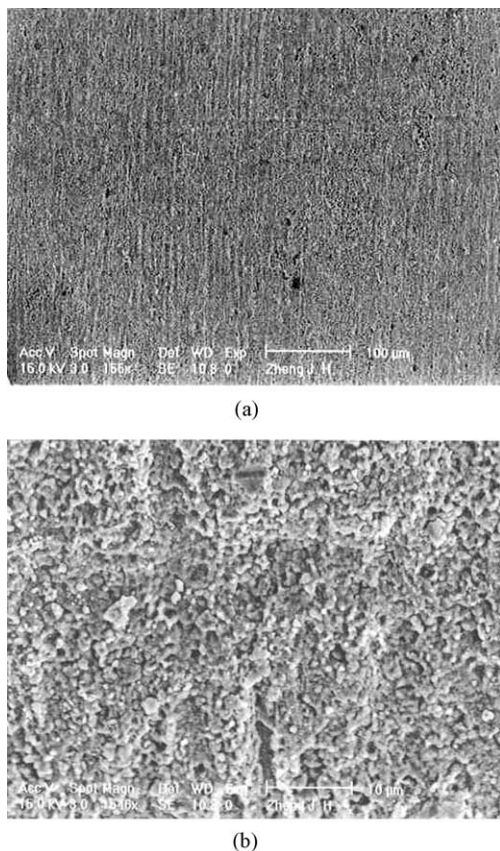Fig. 10. Spalling off of the oxide layer on the inner surface of mock-ups.

Fig. 11. Morphology of the mock-up copper surface underneath the oxide layer.

partly spalled off. As a result, bare (or only slightly oxidized) copper surfaces underneath became visible. The detachment of oxide layer that still remained on the copper surface illustrates again the poor adhesion of the surface layer.

Typical characteristics of the bare copper surface underneath the oxide layer are shown at different magnifications in Fig. 11. Machining traces from mock-up fabrication are still visible (see picture 11a), but the surface looked very rough even with a presence of holes or cavities (see picture 11b). These pictures provide clear evidence that the CuCrZr alloy was attacked during the exposure period to the oxidizing environment containing 5–10 ppm of H_2O_2.

The present investigation shows that the exposure to strongly oxidizing conditions under high incident heat flux led to rapid oxidation of CuCrZr alloy, with the formation of a fairly thick cupric oxide layer after only short periods of exposure. This oxide layer is not always very stable and may spall off, either as a result of thermal or mechanical shock, or due to water flow effects. It remains to be investigated if other water chemistries, i.e. HWC, or alternative water treatments would efficiently reduce the formation of this thick surface oxide layer.

Aside from the detachment of surface oxide layers (i.e. CuO, cupric oxide) as a result of very high water velocities, true flow-induced corrosion as such may seem to be a lesser problem. Although corrosion may be accelerated, no signs of real impingement attack or erosion corrosion became apparent in our different tests.

These results should allow rationalizing the final options for the ITER water chemistry, and all results obtained so far suggest the necessity for strict hydrogen water chemistry (HWC), or for another alternative water treatment, to limit the copper corrosion rate or at least the release of copper into the cooling water circuit.

If high operation temperatures for the divertor cooling water would still be envisaged, it is certainly needed to verify the effectiveness of HWC for reducing corrosion rates of copper alloys at these temperatures (e.g. 250 °C).

Nevertheless, all of these materials tested may be a viable choice if the cooling circuit can be operated at moderate temperatures (say ca. 100 °C), certainly under reducing water chemistries, and provide a low corrosion rates that can be tolerated from the point of view of corrosion product release and accumulation in the circuit.

4. Conclusions

Under very adverse testing conditions, i.e. testing in oxidizing water with a nominal flow velocity of 10 m/s, with fairly high concentrations of hydrogen peroxide (5–10 ppm H_2O_2), 100 °C and intermittent heat loads (~ 10 MW/m^2), followed by cooling cycles under maintained oxidizing conditions, the currently tested ITER reference material, i.e. CuCrZr, has shown

- the formation of black, rather thick surface oxide films (essentially cupric oxide, CuO), even after these relatively short periods of testing;
- this surface layer is rather loosely adherent, and either mechanical or thermal shocks, or fluid flow velocity effects seem to be capable of detaching the oxide layer;
- where the surface oxide layer spalls off, underneath the film a rough surface morphology and some indications of surface attack in this H_2O_2 oxidizing environment become visible.
- It is also not sure how the thickness of the surface oxide layer will evolve over time.

So far, true flow-induced erosion corrosion seems to be a lesser problem. No signs of real impingement attack or erosion corrosion became apparent in our different tests, except the detachment of surface oxide layers possibly as a result of very high water velocities.

These results obtained so far allow rationalizing the final options for the ITER water chemistry, suggesting the necessity for strict HWC, or for another alternative water treatment, in order to limit the copper corrosion rate or at least the release of copper into the cooling water circuit.

Acknowledgements

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