Effect of high-temperature oxidation on the surface properties as applied to quenching of high-temperature bodies

I A Molotova¹, A R Zabirov¹,², V V Yagov¹, E V Terentyev¹, N N Antonov², I M Molotov², A V Tumarkin³ and M M Kharkov³

¹ National Research University "MPEI", Russia, 111250 Moscow, Krasnokazarmennaya, 14
² Joint Institute of High Temperature, Russia, 125412 Moscow, Izhorskaya, 13, Bd. 2
³ National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe sh. 31, Moscow, 115409 Russia

Irina_molotova1705@mail.ru

Abstract. This paper contains the results of studying the surface properties before and after high-temperature oxidation. For this, the plate zirconium samples with chromium, gold and silver coatings were prepared. Cut profiles of the samples were obtained to study the structure of coatings and the thickness of the oxide layer. The measurements of contact angles were carried out. The results showed that a porous heterogeneous oxide layer was formed on the samples after high-temperature oxidation. At the same time, the wettability of the samples was improved. The thickness of the oxide layer on the chrome-coated zirconium sample was the smallest. Using of electroplated silver coating for experiments involving heating to high temperatures seems inappropriate because it was damaged after the oxidation tests. It is assumed that the main factor which influence on the rise of the transition temperature to the intensive cooling regime during quenching is the appearance of the oxide layer, rather than the improved wettability and wickability. High-temperature oxidation leads to the simultaneous formation of an oxide layer with a low thermal effusivity and to an improvement in wettability, therefore the contribution of each of these two effects on quenching can be confused or overestimated.

1. Introduction
Investigation of the cooling process of high-temperature bodies in liquids is of interest for many industries. These include thermal power engineering, metallurgy and nuclear power engineering. For nuclear energy and safety, after the accident at Fukushima in 2011 research works have begun in many scientific centers to find accident-resistant fuel for nuclear power plants (NPP) and to study its characteristics. New types of the fuel and cladding materials of fuel rods are named “accident-tolerant fuel” (ATF). Its concepts are aimed to delay the start of destructive process in the case of accidents by reducing the oxidation rate at high temperatures, as well as by potentially delaying the explosion. It is also necessary to investigate properties of the new materials in the event of a loss-of-coolant accident (LOCA) at NPP. When the core of a nuclear reactor is re-flooded, a film boiling regime takes place. It is characterized by low heat transfer coefficients and cooling rates. For fast cooling of the fuel rods and prevention of a catastrophe, it is necessary to achieve a transition from film boiling to a more intensive
heat transfer regime. It is known that during quenching process, a special regime of heat transfer with a very high intensity may occur [1, 2]. This regime observes under certain conditions even at temperatures of the cooled surface significantly higher than the critical temperature for the cooling liquid.

The properties of the cooled surface significantly influence on the cooling process of high-temperature bodies in liquids, that confirmed by different researches. The surface temperature at which intensive heat transfer regime starts (further – transition temperature \( T_r \)) can be significantly increased by changing in the surface structure, for example, by mechanical or physicochemical modifications. The fact that the rate of cooling processes is influenced by the thermal effusivity of the cooled body is confirmed by cooling experiments of high-temperature samples made of different metals. For example, the copper sphere cooled slower than the nickel and stainless steel [3]. In [4] the process of cooling high-temperature cylindrical samples (which simulate fuel rods) were studied. This experiments also confirm the influence of the cooled body properties on the cooling intensity. In another work [5] experiments were also carried out on the cooling of cylindrical samples in relation to the tolerant fuel concept. Zircaloy sample was cooled faster than stainless steel, copper and niobium due to its relatively low thermal conductivity.

Many authors apparently believe that an increase of wettability of the cooled surface leads to increasing in the \( T_r \). In some works, also used the concept of wickability and determined the effect of this parameter on the \( T_r \) [6]. However, the etched porous surfaces after chemical etching, in addition to superhydrophilicity, also were rough. In [7] it was concluded that the \( T_r \) is significantly influenced by nanoporosity, not only high surface wettability. In other works, the role of superhydrophilicity of the surface during cooling in subcooled water of a cylinder [8] and a sphere [9] was studied. Cooled zirconium samples were fabricated by anodic oxidation. It is reported that the superhydrophilicity had a strong effect at low subcooled temperatures, and its effect decreased at high temperatures.

There is a difficulty in analyzing the influence of the surface structure on heat transfer. Perhaps there is a misleading in the assessment of the wettability effect and the effect of a low thermal conductivity coating (oxide layer) on the rise of the \( T_r \) during cooling of high-temperature bodies. Surface oxidation leads not only to the appearance of an oxide layer with a lower thermal effusivity (\( \sqrt{\rho c \lambda} \)), but also to an increase in its roughness, porosity, wettability. In addition, the results of different quenching studies point to the influence of surface oxidation on heat transfer during cooling of high-temperature bodies. In [10] oxidized zirconium and SiC samples had a higher transition temperature. In another study [11] the \( T_r \) increased due to the formation of the oxide layer during repeated experiments on cooling a high-temperature zirconium sample. It in turn increased the wettability of the sample. The same effect is observed on an oxidized steel sample when quenched in saturated and subcooled water [12]. Based on the large array of our experimental data on the cooling of metal samples in liquids [2-4], an approximate physical model was presented in the paper [2]. In it the influence of the thermal effusivity of a cooled body on the transition temperature was taken into account. The model has confirmed its efficiency for cooling of high-temperature samples made of various metals.

Direct contact of liquid and solid surface is impossible during film boiling, so wettability can hardly affect cooling at cooled surface temperatures above critical for the cooling liquid. It is possible only short local liquid-solid contact. Therefore, wettability can be a secondary factor, which can increase by the formation of the oxide layer on the surface. In [13] oxidized samples also had a higher \( T_r \) in comparison with unoxidized samples. Capillary wicking in unoxidized Zircaloy-4 was higher than in the Zircaloy with chromium coating. According to the authors' assumption, it is due to the oxidation of Zircaloy-4 in the environment. In addition, oxidized surfaces have greater roughness than non-oxidized samples, which also leads to a faster transition to intensive heat transfer regime for all samples.

As is known, cryoliquids have good wettability. Thus, during quenching in cryoliquids (usually liquid nitrogen), a change in the \( T_r \) can be caused only by the thermophysical or geometrical properties of the cooled body or coatings [14, 15].

On the other hand, coatings to protect against the formation of the oxide layer are of great interest. With regard to cladding materials of fuel rods, the thickness of the oxide layer limits the service life of a nuclear reactor. Based on this, zirconium samples (since zirconium is a material for fuel cladding) with
coatings with different thermophysical properties were selected for the experiments. Tests were carried out on high-temperature oxidation of these samples, followed by cooling in water. These experiments were conducted in order to study changes in wettability after high-temperature oxidation of the samples, as well as to study the structure of coatings before and after tests on high-temperature oxidation.

2. Test samples and methods
For the experiments, flat round samples of zirconium E110 with a diameter of 12.5 mm and a thickness of 1 mm were prepared. Three types of coatings were applied to the samples: chromium with a thickness of about 1 µm, gold and silver with a thickness of about 3 µm. Before applying the coatings, the samples were polished. Chromium was deposited by magnetron sputtering, details on the sputtering method are presented in [16, 17]. The dense coating was obtained as a result, an arithmetic average profile deviation (Ra) was 1 µm (Figure 1a). Gold and silver were applied by electroplating (Figure 1b, c). Ra was 0.5 and 1.7 µm for gold and silver coatings, respectively. Figure 1 shows the results of optical microscopy of the surface of zirconium samples with these coatings.

![Figure 1](image-url)

Figure 1. Optical microscopy of the zirconium samples with coatings of (a) chromium; (b) gold; (c) silver.

Before the experiments, the contact angles were measured for the samples with different coatings. The oxidation of the samples was carried out in a crucible melting furnace, which was preheated to 700 °C. The samples were fixed on a stainless steel wire and immersed in the crucible for 30 minutes. The heated samples were cooled in water at room temperature (24 °C). Thereafter, the high-temperature
oxidation test was repeated. Between and after oxidation tests, contact angles were also measured. Also, part of the samples was cut for studying the structure and thickness of the coatings and the thickness of the formed oxide layer. It was done before and after oxidation tests and cooling in water.

3. Results and discussion

It should be noted that zirconium with chromium coating is considered as a tolerant material for fuel rods in nuclear reactors, so the oxidation of this sample is of particular interest for nuclear power. Cut profile of the zirconium sample with chromium coating showed that the thickness of the chromium layer is 1 μm (Figure 2a). The coating was enough uniform and non-porous. After oxidation tests, a layer of porous and heterogeneous oxide formed on the sample surface with a thickness of 4-7 μm (Figure 2b).

![Figure 2. Cut profiles of the zirconium sample with chromium coating before (a) and after (b) high-temperature oxidation tests.](image)

The thickness of gold electroplating coating on zirconium was about 3 μm (Figure 3a). After oxidation tests, oxide layer also had pores. The thickness of the oxide layer was greater than that of the chromium-coated zirconium and was about 10 μm (Figure 3b).

![Figure 3. Cut profiles of the zirconium sample with gold coating before (a) and after (b) high-temperature oxidation tests.](image)

The thickness of silver electroplating coating on the zirconium was also about 3 μm (Figure 4a). For better adhesion of silver to zirconium, a copper sublayer with a thickness of 1-3 μm was applied, which is visible in Figure 4a. The silver coating did not pass the high-temperature oxidation tests, and cracks
were observed on the coating with a thick oxide layer (thicker than 10 μm) (Figure 4b). Apparently, the coating burned out during experiments on high-temperature oxidation. So, silver electroplating coating is not suitable for protecting of the samples that will be heated to high temperatures of about 700 °C.

Figure 4. Cut profiles of the zirconium sample with silver coating before (a) and after (b) high-temperature oxidation tests.

Wettability of the samples was measured before the high-temperature oxidation tests (Figure 5a), between oxidation, and also after experiments (Figure 5b). In Figure 5 it is clearly seen the improved of the wettability on the oxidized samples. A drop of water spreads very rapidly when it is deposited on the sample after high-temperature oxidation tests. The average results of the contact angles were summarized in Table 1. As evidenced by the results, the contact angles for all types of coatings on the flat zirconium samples decrease several times after the oxidation of the samples.

Figure 5. Wettability of the samples before (a) and after (b) two high-temperature oxidation tests, from left to right: chromium, gold, silver coatings.

| Table 1 | Contact angles of zirconium samples with coatings before and after high-temperature oxidation tests. |
|---------|--------------------------------------------------------------------------------------------------|
|         | Zr with chromium coating | Zr with gold coating | Zr with silver coating |
| Before oxidation | 58 | 59 | 47 |
| Between oxidation tests | 35 | 30 | 38 |
| After oxidation | 9 | 17 | 17 |
Thus, the oxide layer with low thermal effusivity was formed on all tested samples. In this case, the thinnest oxide layer was on the zirconium sample with chromium coating. High-temperature oxidation, in turn, has led to improved wettability for all types of coatings (especially for chrome coating). It supports the idea that the formation of the oxide layer usually leads to improved wettability.

4. Conclusion
For the experiments on high-temperature oxidation, the flat round zirconium samples with different coatings were prepared: chromium, gold and silver. After two cycles of high-temperature oxidation in a crucible furnace, porous and heterogeneous oxide layers formed on all samples. The silver coating did not pass these tests. It was suggested that the increasing of the transition temperature to intensive cooling regime during quenching is influenced by the growth of the oxide layer, more precisely, its thermal effusivity. In this case, the wettability is a secondary factor, which growth is caused by the formation of this oxide layer. This hypothesis was confirmed by the conducted experiments. In the experiments presented in this paper the formation of the oxide layer on samples with different coatings led to an improvement in their wettability (the contact angles decreased from 50–60° to 10–20°). Further research will focus on experiments on cooling high-temperature cylindrical zirconium samples without and with different coatings in relation to the tolerant fuel concept (including chromium-coated zirconium). These studies will make it possible to experimentally investigate the transition temperatures to the intensive cooling regime and to verify the developed approximate model of the occurrence of the intensive heat transfer regime during cooling of high-temperature bodies in liquids.

Acknowledgments
This work was supported by the Russian Foundation for Basic Research, Grant No. 19-38-60057.

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