Research Article

Development of the technique for determination the rate of oxidation of structural steels in heavy liquid metal coolants*

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Abstract

The article considers the main methods for studying the process of oxidation of structural steels and evaluating their corrosion resistance in heavy liquid metal coolants (HLMC) under static and dynamic conditions. It is shown that the main disadvantage of these methods is the impossibility of evaluating the results in real time. The authors propose a new method for the experimental determination of the oxidation rate of steels in molten HLMCs, which makes it possible to measure the reaction rate without depressurizing the plant, by periodically injecting air doses of a known volume and monitoring its response time. As additional data in the research methodology, the results of a chemical-spectral analysis of the coolant and slags were provided after the experimental campaign completion as well as a metallographic analysis of steel samples to determine the oxide coating thickness and its comparison with the calculated value for the integral oxygen assimilation by the system. To implement the methodology, a laboratory facility was proposed, equipped with an oxygen thermodynamic activity (TDA) sensor of the RF-IPPE design. The sensor is certified by Gosstandart of Russia (certificate RU. 31.002 A No. 15464), registered in the State Register of Measuring Instruments (No. 25282-03) and approved for use in the Russian Federation.

Introduction

The working life of structural steels for reactor plants with HLMCs is largely determined by the nature and regularities of oxidation of their internal surfaces by oxygen dissolved in the coolant (Balandin and Markov 1961, Gromov and Shmatko 1997, OECD/NEA 2007). At the present stage,
the development of reactor facilities with HLMCs requires numerical modeling of ongoing processes and predicting the life of structural steels (Alekseev and Orlova 2011).

The purpose of this work is to analyze the main methods for studying the oxidation process and to develop a procedure for the experimental determination of the oxidation rate of structural steels in HLMCs.

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Analysis of existing methods for determining the oxidation rate of structural steels

Experimental methods for determining the steel oxidation kinetics are not numerous: they are generally limited to the exposure of samples in the coolant under given conditions with a subsequent analysis (metallographic, weight, radiographic, etc.) of the scale obtained. As an experiment is conducted, samples are jigged to provide intermediate points on the kinetic curve, which, as a rule, represents the scale thickness-time dependence (Lipetsky and et al. 1985, Zhuk (1976), Kofstadt 1969, Evans 1962, Kubashevsky and Hopkins 1955). Without going into the subtleties of such experiments and interpretation of their results, note that these techniques are used for studying the oxidation process of solid metals both in gas media and various metallic melts.

The main methodological difficulty in studying the process in metallic melts is maintaining the coolant oxidation potential.

In static experimental plants (Martinelli 2011), the melt is rapidly depleted in oxygen due to its low solubility in a liquid metal and the relatively high rate of its consumption by the steel surface (for several tens of minutes).

Tests in conditions of non-isothermal circulation facilities that to some extent imitate processes in the reactor system circuits make it possible to keep for a long time the oxygen concentration in the coolant due to the action of an internal constant oxygen source and oxygen transfer with the coolant flow to the location of samples (Rusanov and et al. 2003). Moreover, along with the oxygen transfer to the surface of structural materials, components of steel are transferred in the opposite direction, i.e., into the coolant, where they are also oxidized with the corresponding unaccounted oxygen consumption. Such tests are very costly, because they require a significant consumption of electricity and continuous monitoring of the equipment for a long time.

The main drawback of traditional test methods (in static or circuit facilities) is that they yield results only in *post-factum* mode. In addition, at the end of such experiments, it is often impossible to balance the supplied oxygen and oxygen consumed to form a protective film on the surface of samples.

Method of the experimental determination of the oxidation rate of structural steels

To study the steel oxidation process in HLMCs, a new method is required to determine the values of the oxidation rate without depressurizing the unit directly during the experiment (*on-line*) and without waiting for the samples to be extracted. In addition, the method should make it possible to maintain or at least control the oxidation conditions (temperature and oxidation potential). The sensitivity of this method should not be inferior to that of traditional methods and not exclude, but complement them, i.e., the integral quantitative result of the process is to be estimated by not only this new method, but also by traditional ones, i.e., metallography, x-rays, spectroscopy, etc. (Martinelli 2011, Rusanov and et al. 2003, Mulier 2008, Molokanov and et al. 2002).

To maintain the system oxidation potential, an oxygen source is required that can be external or internal. In any case, it is necessary to know its power (or the rate of oxygen supply to the coolant). The ideal solution would be an oxygen supply device, the power of which would be known and regulated. Using such a device, it would be possible to select the power of the source in a way corresponding to the drain power and ensuring the constancy of the oxygen thermodynamic potential in the coolant during the experiment. Technically, such sources are oxygen pumps based on oxygen-ion solid electrolytes. However, at temperatures typical for steel testing, the specific power of such pumps remains low enough for oxygen flows, which significantly reduces the possibilities of their practical application.

At the same time, it is possible to organize a process of cyclic increase/decrease of the oxidation potential by periodic oxygen injections into the system. Measurements of the oxidation potential with simultaneous measurements of the average reaction rate make it possible to compare the data and to reveal the dependence of the reaction rate on the oxidation potential $q_0 = j(p_{02})$ at a constant temperature.

Oxygen can be periodically injected into the coolant by two alternative ways, i.e., by injecting:

– gaseous oxygen through the interface of the coolant with the gaseous phase;
– oxygen through dissolving a solid-phase source, for example, from granular lead oxide.

It is known that any chemical process can be controlled by the rate of change in the mass of any reagent or by the rate of accumulation of reaction products. If the relationship between reagents and reaction products is known (stoichiometry), then the answer to the question by which reagent the process should be controlled becomes obvious: by the one that is more convenient.

Components of steel and reaction products – oxide films – are internal elements of the system under consideration, and their quantitative characteristics can be measured without opening the system only if there are means of nondestructive testing. But today there are no such means.

To quantify the oxidation rate of steels, both proposed methods require that the injected oxygen amount and the system response time should be measured.

The system response time (required to assimilate the supplied oxygen dose) can be determined by readings of the oxygen activity sensor (OAS) developed at the JSC "SSC RF-IPPE" (Chernov and et al. 2003). The supplied dose as-

similation time is the time from the oxygen supply to the return of the OAS readings to the initial level. The sensor electrical signals (E_{OAS}) can be converted into the oxygen activity, oxygen partial pressure, or oxygen concentration in the coolant by known relationships (Kulikov 1986).

The amount of oxygen supplied in the first way is fairly easy to registered by means of a calibrated volume of an oxygen-containing gas mixture, for example air. The use of atmospheric air does not require developing additional equipment for preparing and storing gases. The air dose value is easily measured by the volume of the vessel in which it is located and atmospheric pressure.

The simplest devices for injecting calibrated gas volumes are chromatograph calibration syringes usually supplied in STA sets. However, these syringes are designed for a single volume (usually 1 cm^3) and do not allow the injected gas dose to be varied. At the same time, medical syringes have a wide range of sizes (from 0.5 to 100 cm^3) and can be successfully used for measuring air portions.

The mass of oxygen in 1 cm^3 of air is calculated from the oxygen molecular weight (32 g/mol), its volume concentration in air (0.21% vol) at a pressure of 1 atm (760 mm Hg) and is:

$$m_O = 0.21 \times 32 /(22.4 \times 1000) = 0.0003 \text{ g/cm}^3.$$

Natural atmospheric pressure fluctuations within ±400 Pa (~ 30 mm Hg) can lead to an error in determining the air mass at a level of no more than 0.5% rel.

The supplied dose assimilation time Dt = t_{start} − t_{fin} is measured by a chronometer taking into account changes in the oxygen activity sensor readings, as the time for the readings to return to the initial level $E(t_{start}) = E(t_{fin})$, where t_{start} is the moment of injecting an air portion; t_{fin} is the moment of the OAS EMF returning to the initial level.

The average oxygen flux measured in this way can always be converted into an iron stream or an oxide stream in accordance with stoichiometry. The integral of the total oxygen amount supplied can be used for reducing the material balance after the test is completed.

Thus, the principal scheme for measuring the oxidation rate of steels that come into contact with HLMCs at a given temperature is as follows:

– in a tight system containing a molten liquid metal with steel samples of a known surface area, the required volume (mass) of oxygen (or air) is supplied;
– using the oxygen activity sensor, the EMF value of the sensor galvanic cell is fixed at the time of the oxygen dose;
– using a chronometer, the time is recorded for which the sensor readings return to the initial EMF value.

The supplied oxygen mass (m_O) during its assimilation (Dt) by the steel surface of a known area (S) will be the desired value of the specific oxidation rate for oxygen:

$$q_O = m_O/(Dt \times S), \text{ g/(h} \times \text{cm}^2).$$

This equation shows the limiting possibilities of the method for determining the oxygen flux.

The minimum oxygen dose mass is ~ $(1.5-3) \cdot 10^{-4}$. The steel surface, which can be provided in a static facility, is ~ $n \times 100$ cm^2. If such a dose is actuated in about an hour, the oxygen flow will be about 10^{-6} g/(cm$^2 \cdot$h), and if the response time increases up to 10 hours, the oxygen flow will be ~ 10^{-7} g/(cm$^2 \cdot$h).

A further sensitivity increase, for example, up to 10^{-8} g/(cm$^2 \cdot$h) necessitates, other conditions being equal, increasing the duration of measurements by one more order. This increases the requirements for the plant integrity, since forced compensation of shielding gas losses, as a rule, leads to injecting uncontrolled oxygen amounts into the facility. It is also possible to increase this method sensitivity by developing the steel surface. However, in the limited space of a static facility, significant progress in this direction is problematic.

By way of comparison with traditional methods for studying oxide film thicknesses (their measurement error usually does not exceed 1 μm), let us estimate the oxide film effective thickness for a single measurement of the oxygen flux in the proposed procedure. Taking into account the density of stoichiometric crystalline magnetite (5.2 g/cm^3) and its chemical formula, we find that its oxygen density is ~ 1.4 g/cm^3. Then, for a characteristic surface area of the sample of 100 cm^2, the film effective thickness, when an oxygen portion of 1.4×10^{-4} g is assimilated, is ~ 10^{-2} μm, i.e., the sensitivity of this method is approximately two orders of magnitude higher than the traditional one.

The second way of injecting oxygen using solid-phase oxides can be organized from both an external or internal source pre-located in the system under study. For injecting oxygen from an external source, it is required to develop and manufacture a special airlock preventing the unaccounted oxygen from entering the reaction chamber.

A simpler option is to place a solid-phase oxygen source inside the reaction chamber, for example, in a gas volume, with the possibility of moving it vertically to periodically immerse the lead oxide in the coolant melt.

The sensitivity of the method involving a solid-phase oxygen source is determined by balancing the two processes, i.e., lead oxide dissolution and steel oxidation. In conditions of circulation facilities, i.e, at relatively definite rates of the coolant flowing around granulated lead oxide fillings corresponding to reactor plant conditions, the lead oxide dissolution rate has been studied quite well (Askhadullin and et al. 2003). However, in static, relatively undefined hydrodynamic conditions, when granules are flowed around exclusively in natural circulation mode, this method requires additional experimental justification and calibration.

It is convenient to calibrate the solid-phase oxygen injection method by comparing the results of supplying gaseous oxygen and oxygen from a solid-phase source by the EMF change value, when the system is affected by the first and the second methods.

Implementation of the developed method for the experimental determination of the structural steel oxidation rate

Taking into account the formulated requirements, an experimental facility has been developed to implement the proposed method for measuring the oxygen flow (the oxidation rate). Its schematic diagram is shown in Fig. 1.
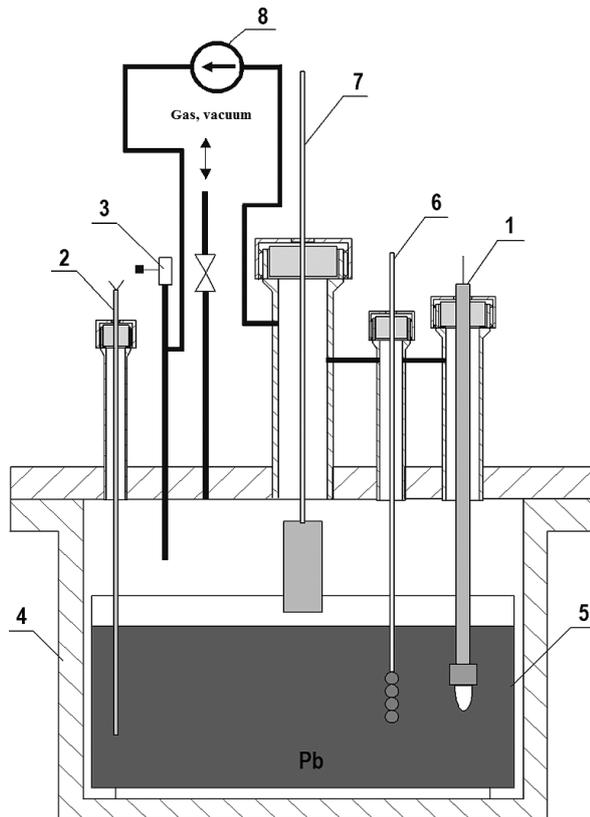
Figure 1. Schematic diagram of the facility for studying steel oxidation in HLMC: 1 – thermodynamic activity sensor; 2 – thermocouple; 3 – sample valve; 4 – reaction tank; 5 – steel beaker with the coolant; 6 – rod with PbO pebbles; 7 – rod with steel samples; 8 – gas blower

The facility consists of a cylindrical hollow reaction chamber containing a metal beaker, made from the steel under study, with the molten coolant ($m \sim 5$ kg). In the removable cover of the chamber there are several openings with tubes for placing coolant monitoring sensors, shielding gas inlet/outlet and other equipment necessary for research. Cylindrical witness-samples for subsequent metallographic analysis are placed on the rod when the facility is mounted.

The unit is equipped with an oxygen thermodynamic activity (TDA) sensor designed at the JSC "SSC RF-IP-PE". The developed sensors are certified by the State Standard of Russia (certificate RU. 31.002 A №15464), registered in the State Register of Measuring Instruments (No. 25282-03) and approved for use in the Russian Federation. In the overwhelming majority of conducted campaigns, sensors with the system $\{Bi\}$-$<Bi_2O_3>$ as a reference electrode were used.

At the stage of commissioning tests, two methods for supplying oxygen were tested: in the composition of air portions of a known volume or in the composition of lead oxide spheroids.

By way of example, Fig. 2a presents the results of the effect of 20 ml air doses on the Pb-Bi melt in contact with EP-823 steel; Fig. 2b shows the effect of 5 and 10 ml air doses on the Pb-Bi melt in contact with EP-302 steel, at two initial levels of the coolant oxidation potential.

The main difficulties in implementing the solid-phase method of dosed oxygen injection are associated with the reliability of the estimated oxide dissolution rate. In particular, it is known that the process of dissolution of lead oxides is characterized by the determining effect of the oxygen transport diffusion stage in a liquid metal. This means that the hydrodynamic conditions for a liquid metal flowing around oxides significantly affect the dissolution rate. The uncertainty in hydrodynamic conditions typical of static facilities can lead to uncertainties both in the dissolution rate and in the steel oxidation rate estimations. For this reason, an attempt was made to calibrate oxygen doses injected by means of solid oxides by comparing the results achieved with the results of using the gas-phase oxygen injection method.
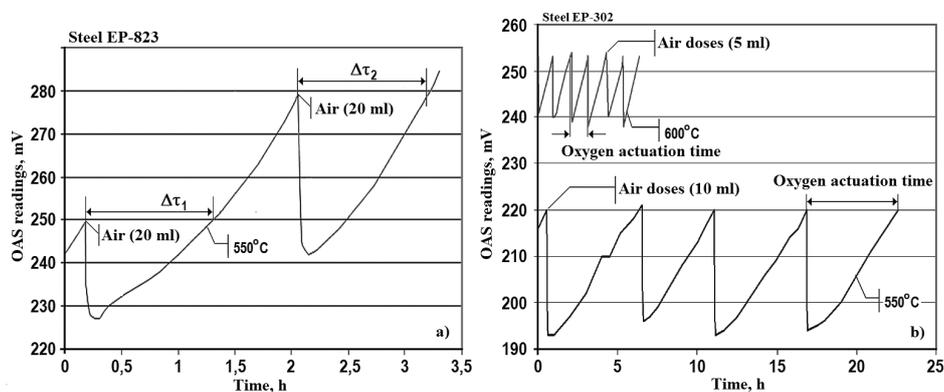
Figure 2. The oxidation effect of air doses on (a) EP-823 steel at 550°C in the lead coolant and (b) EP-302 steel at 550 and 600°C in the Pb-Bi coolant

Fig. 3 shows the dynamics of OAS readings with periodic oxygen injections by the gas-phase and solid-phase methods. Despite some differences in the coolant oxidation rates, which characterize the intensity of oxygen injected to its volume when air is supplied and when solid granular lead oxide is immersed, it turned out that the coolant deoxidation kinetics, which characterizes oxygen consumption by steel, remains the same (which means the equality of the effect of oxygen flows on steel oxidation). This allows us to relate the solid-phase oxide residence time in the coolant with the amount of oxygen supplied to the coolant and use this circumstance to determine the calculated value of the supplied oxygen amount when the oxides were immersed in the coolant.
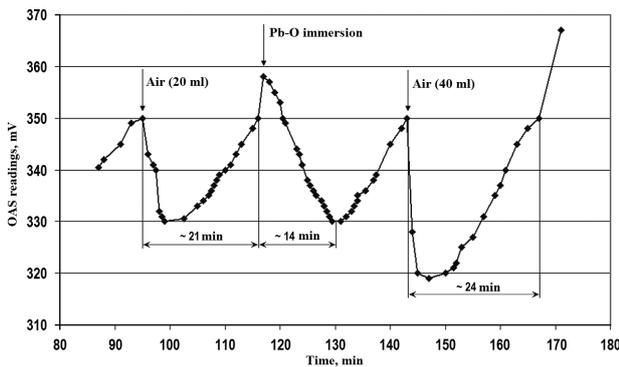
Figure 3. The OAS readings at the dosed oxygen input by gas-phase and solid-phase methods (lead temperature = 615°C)

By way of example, Fig. 4 shows the results of determining the oxygen flux consumed by steel as the total air volume consumed to maintain the fixed coolant oxidation potential as the experiment duration function (Ivanov and et. al 2005). The oxidation potential was maintained first by the gas-phase method and then by the solid-phase method, when the oxide immersion time was varied and the equivalent amount of air was calculated by the preliminary calibration results. Note that the equivalence of
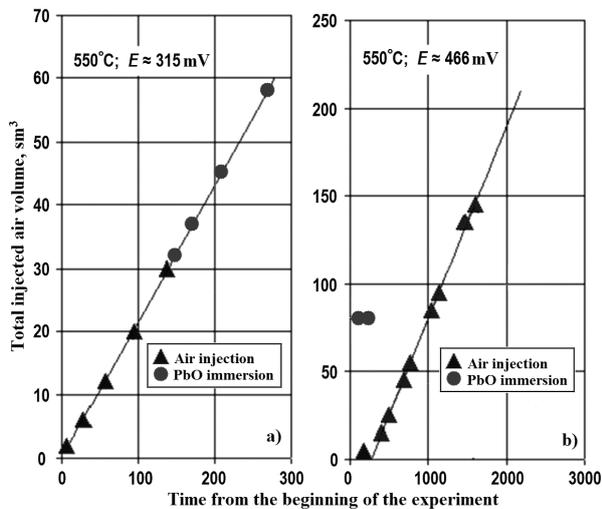
methods for injecting oxygen into the coolant has been proven at relatively high values of the coolant oxidant potential (in this example, the OAS readings = $E \gg 315$ mV).

Using the calibration results of the solid-phase method for injecting oxygen into the coolant in the range of sufficiently low oxidation potential yields wrong results. Figure 4b shows the dependences of the integral oxygen amount injected into the coolant while maintaining a predetermined level of the oxygen thermodynamic activity ($E \gg 466$ mV: triangular markers are used for the gas-phase oxygen injection method and round markers indicate the use of solid phase oxides). It can be seen from the graph that the calculated values of oxygen obtained from the time of immersion of oxides in the coolant do not correspond completely to the data on the oxygen amount injected using the gas-phase method. The actual amount of oxygen injected using the solid-phase method turned out to be substantially less than the calculated value.

An analysis of the causes for the observed deviations showed that a decreased rate of oxygen supply from oxides to the coolant at its low oxygen thermodynamic activity is due to the presence of iron impurities in the coolant. Their high thermodynamic activity under these conditions provokes the formation of a layer of mixed iron oxides on the surface of the lead oxide, preventing oxygen from passing to the coolant.

This lead oxide "poisoning" effect was confirmed after the end of the pilot campaign conducted using lead oxide spheroids. The chemical and X-ray diffraction analyzes of spheroids have shown the presence in their surface layers of a significant amount of iron in the oxide form.

Thus, taking into account the results of the conducted experiments, the gas-phase method can be recommended as the main one for dosed oxygen injections into the coolant when implementing the proposed method for studying the steel oxidation kinetics.

Conclusion

To study the processes of oxidative interaction between lead-based heavy liquid metal coolants and structural steels, an experimental method was proposed for determining the intensity of dissolved oxygen consumption by steels in the coolant.

The method consists in fixing the return time of the coolant oxidation potential (oxygen TDA sensor readings in the liquid metal melt) to the initial level after injecting a known portion of oxygen into it. Correlating this quantity of oxygen with the total contact surface of the coolant with the steel under study and the time of its assimilation makes it possible to calculate the average steel oxidation rate for a given period of time.

The sensitivity evaluation of this technique shows that it is at least two orders of magnitude greater than the methods based on measurements of the oxide film thickness.

A laboratory facility has been created to implement the proposed method for measuring the oxidation rates of steels in heavy coolants and two methods for dosed

Figure 4. Comparison of the results of using the solid-phase oxygen injection method at $T = 550$°C and various oxidation potentials of the lead coolant: a) – $E \gg 315$ mV; b) – $E \gg 466$ mV

oxygen injections into the coolant using gas mixtures and solid-phase oxides have been experimentally tested.

It is shown that the gas-phase method is more preferable: this method is recommended as the main one for further use.

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