

CORROSION PROCESSES IN ZIRCONIUM FLUORIDE – SODIUM FLUORIDE MELTS.

STUDY OF SHORTCUT CELL $C/(ZrF_4 - NaF)_{EUT}/HASTELLOY$

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Time dependencies for the parameters (current, voltage, inner resistance) of shortcut galvanic cell Hastelloy-carbon material have been studied in NaF-ZrF₄ eutectic melt at 600...650°C. Analysis of these data, together with the data on polarization of separate electrodes at open circuit conditions, showed that shortcut current is related to the rate of corrosion of the alloy contacted with carbon, if Zr metal is absent in the system. In presence of Zr, the current corresponds to the rate of zirconium reaction with the melt (related to unit surface of the Hastelloy electrode), and can be used for studies of dissolution kinetics of Zr metal in the melt. It was found that contact of the alloy with carbon material results in the increase of corrosion rate both in pure eutectics and with the additives of LaF₃. Presence of Zr metal suppresses the corrosion process.

INTRODUCTION

It is known that Ni-Mo alloy (trademark Hastelloy) are relatively stable in zirconium fluoride molten mixtures and can be used as the material for technical applications of such melts, in particular, in nuclear power technologies. That is why studies of its corrosion resistance in such media are of practical interest.

Corrosion of Hastelloy has been studied earlier by the electrochemical technique, X-ray analysis, SEM and metallography [1]. Corrosion currents were found to be about 10⁻² mA/cm² depending on the preliminary heat treatment and irradiation. This is fairly good stability for most practical applications.

The above mentioned data correspond to the behavior of the alloy contacted with the melt only. However, the metal in some important cases is in long-term contact with graphite or other carbon material. One can expect the differences in corrosion resistance of the alloy because of the formation of electrochemical couple working as a corrosion shortcut galvanic cell. This paper presents some results on the corrosion behavior of Hastelloy in contact with carbon material. Processes in pure ZrF₄-NaF eutectic melt and in the presence of the LaF₃ and Zr metal additives were studied.

EXPERIMENTAL

Linear sweep voltammetry was used for studies of corrosion processes at separate electrodes. The voltammograms were taken by means of the PC governed Potentiostat PI-50 at scan rate 2 mV/s vs. classy carbon reference electrode (RE) in case of the alloy and vs. Hastelloy (H) RE when C electrode was studied.

Long-term experiments with the electrochemical cell $C/(ZrF_4 - NaF)_{eut}/H$ were performed in glassy carbon or graphite (CC composite) crucibles where the walls served as a C electrode (~35 cm² area was in contact with the melt). Hastelloy plate of 2cm² area was used as second electrode.

The open circuit voltage was measured with high input resistance electronic millivoltmeter V7-21. Milliamperimeter with low inner resistance was used for measurement of shortcut current of the cell. The cell's resistance was checked with AC bridge R5083, frequency was 100 kHz.

RESULTS AND DISCUSSION

Several electrochemical reactions should be considered in the analysis of the processes in the cell:

1. Reduction of zirconium (IV) to low valence compounds. Though the process is a complex multi-step one [2], we denote it by the simplified reaction:



This is the main cathode reaction on both electrodes.

The reaction (1) could be reversible. That is, we should take into account the reverse (anode) reaction after the accumulation of significant amount of low valence species in the melt:



2. The anode process on the alloy electrode is the electrochemical oxidation of the metal:



where Me = Ni (main component) or Mo, Cr, Ti, Fe (doping metals).

3. No reductant species other than carbon are present in the system at the initial time period; then the oxidation of carbon should be the main anode reaction at C electrode of the cell. Basically, it must be the electrochemical fluorination of the carbon¹:



The reactions (1) and (2) proceed with equal rates in open circuit conditions. The polarization curves of the electrode plotted in semi-logarithm scale can be used for calculation of stationary potentials and corrosion currents. Fig. 1 shows an example of such plot.

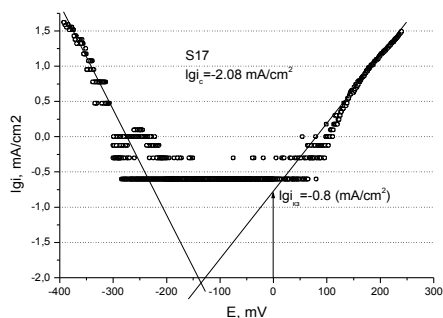


Fig. 1. Typical corrosion diagram of Hastelloy (vs. glassy carbon RE) in a fresh melt $ZrF_4 - NaF$, $600^{\circ}C$. The arrow shows an expected shortcut current (see below)

The curves in Fig. 1 were taken vs. GC reference electrode. It was noticed that, in freshly prepared melt, the stationary potential, which can be determined at intersect point of the linear branches of cathode and anode curves, attains a value close to -200 mV. In course of the long-time exposure of the melt in carbon container, the potential gradually shifts to more positive values (Fig. 2).

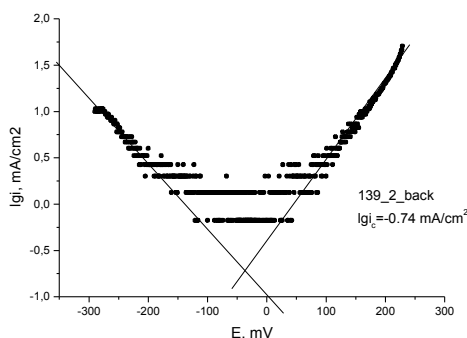


Fig. 2. Corrosion diagram of the alloy sample after prolonged treatment in the melt for several days

Gradual displacement of the stationary potential toward positive values was also found in the experiments where OCV of the cell was measured for several days (Fig. 3). Disregarding the transient processes after melt-

¹ The side reaction $C + O^2 = CO + 2e^{-}$ is also possible if the presence of oxide compounds in the melt cannot be neglected; this possibility should not effect our analysis of the problem.

ing the electrolyte, one can see almost linear time drift of the potential to negative side.

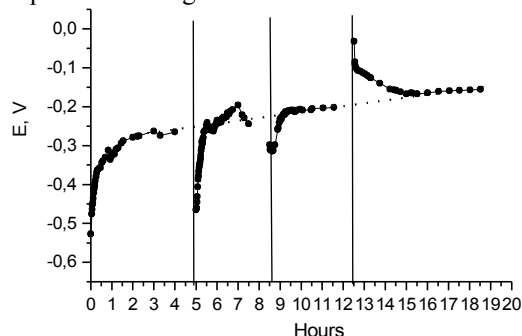


Fig. 3. Stationary potential of the alloy vs. GC measured in daytime for 4-day period. The transients after the vertical lines result from the termination of the process when the electrolyte was repeatedly crystallized and melted again

In our opinion, such drift of the potential vs. GC electrode results rather from the change of GC potential than the metal one. Polarization curves of carbon electrode vs. the alloy RE, Fig. 4, support this conclusion.

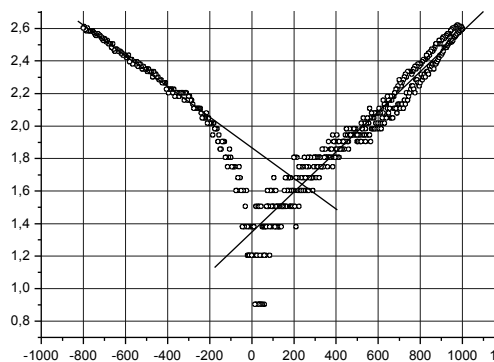


Fig. 4. Semi-logarithm plot of the polarization curves of GC electrode vs. H RE

Linear parts of the dependencies in Fig. 4 intercept at the potential value near $+200$ mV vs. H, which is consistent with the stationary potential difference obtained from the polarization curves of the alloy vs. GC electrode, Fig. 1. However, the current densities on GC electrode are much higher, which evidences essentially larger rates of the electrochemical reactions at this electrode. These reactions in a fresh electrolyte have to be the oxidation of carbon (3) and reduction of zirconium (IV) (1).

Upon a time, such processes on the carbon electrode, with its large surface area and high rates of electrochemical transformations, should result in the accumulation of $Zr(II)$ low valence species in the bulk and, accordingly, to development of the parallel reaction of its anode oxidation (1a). It means that, in open circuit conditions, the potential of GC electrode should approach the value of equilibrium potential of $Zr(IV)/Zr(II)$ couple, which, in turn, is the more negative the higher is the concentration of $Zr(II)$ species in the electrolyte.

Thus, the potential of GC electrode becomes more negative due to the accumulation of low valence $Zr(IV)$

reduction products in the melt. It manifests itself experimentally as the drift of the potential of alloy vs. GC toward more positive values comparatively to the starting point (fig. 2,3).

The potentials of both electrodes approach each other when the cell is shortened. The potential difference then should be determined by the value of shortcircuit current and inner resistance of the cell:

$$\Delta\varphi = I_{sh} R. \quad (4)$$

The inner resistance was periodically checked in course of the experiments. The results are given in Fig. 5.

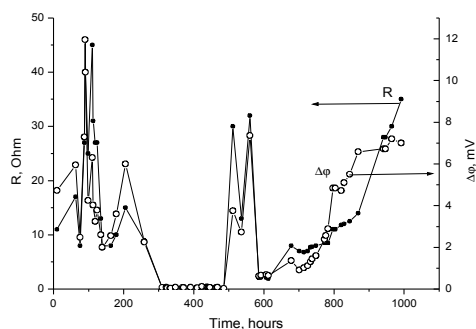


Fig. 5. Time dependencies of inner resistance and ohmic drop on the cell (-)C/(ZrF₄-NaF)/H(+), in long-time continuous experiments. Temperature 600°C

As follows from the data above, the cell's resistance is changing from tenth to several tens of mV in a complex manner.

Meanwhile, the potential difference, calculated from experimental data by the formula (4), is of a few mV only. Since the value of OCV is of 2 orders higher, we can neglect the ohmic potential drop considering the potentials equal for both electrodes when the cell is shortened.

Turning back to the polarization curves of separate electrodes (Fig. 1-3), two important points must be emphasized. First, as it was already mentioned, partial current densities at stationary potential are much larger for GC than for the H electrode. Second, the surface area for GC is also much larger (the ratio of GC to H surfaces in the experiments was 12-15). Thus, it is evident that shortening the cell practically could not effect the potential of GC, while the potential of H electrode would change and attain the value almost the same as the open circuit potential of GC electrode.

From these considerations we can estimate the shortcircuit current from the polarization curves of H electrode vs. C as the current at zero potential. Analysis of the data available shows that shortcircuit current density (per unit surface of H electrode) should be about 100...200 mcA/cm² (for example, 160 mcA/cm² for the sample of Fig. 1). The direct measurements, which are represented below, confirm this conclusion.

Fig. 6 shows the time dependence of shortcircuit cell operated continuously for about 2 months. The dynamics

of system is rather complicated – non-linear oscillations are observed with the period about 200 hours. As it was shown in [3], such behavior of an electrochemical system may result from the effect of feedbacks between sub-systems (electrodes), which are interconnected via the bulk of the electrolyte.

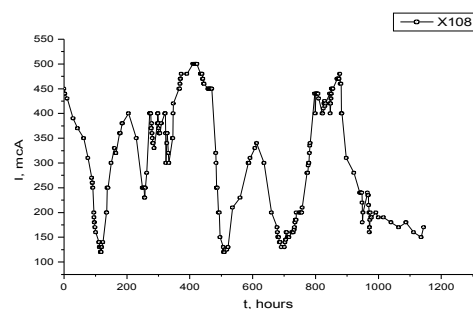


Fig. 6. Time dependence of shortcircuit current of the cell (-)X108/ZrF₄-NaF/C(+), Temperature 600°C, S_c = 35 cm², S_H = 2.5 cm²

In such situation, the time constant of the interaction, which approximately corresponds to the period of oscillations (if the conditions exist for its development), can be determined from the formula

$$T \approx \frac{2 \cdot \pi \cdot \delta \cdot V}{D \cdot \sqrt{S_c \cdot S_a}}, \quad (5)$$

where V is a bulk volume of the electrolyte, δ the thickness of diffusion layer; D the diffusion coefficient, and S_c, S_a the surface areas of electrodes.

The calculations by this formula show that, in case of “common” diffusion through the diffusion layers in molten electrolytes (the order of values: δ~10⁻² cm D~10⁻⁵ cm²/s), the oscillation period should be about 10 hours, which is much less than observed by an order of value.

Reasons for such disagreement could be an increase of diffusion distance (δ) or decrease of diffusion coefficient D or both of these. We assumed that the diffusion processes could be retarded due to its occurrence not only in the melt but in solid also.

To check this assumption, we prepared a cross-section of the electrode after durable exposition in melt (Fig. 7).

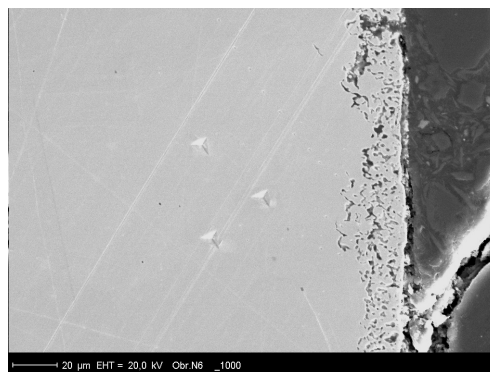


Fig. 7. SEM photograph of cross-section after durable exposure in ZrF₄-NaF + 6,7%LaF₃ melt

In Fig. 7 one can see, under the layer of frozen electrolyte, a thin (~1mm) film of reaction products, which could affect the process. However the investigation of the composition of alloy along the cross-section evidences another most probable reason (Fig. 8).

As follows from the data of Fig. 8, the doping metals (Cr, Al, Ti) are oxidizing rather than the main component Ni. Hence, its diffusion to the surface should effect the overall kinetics.

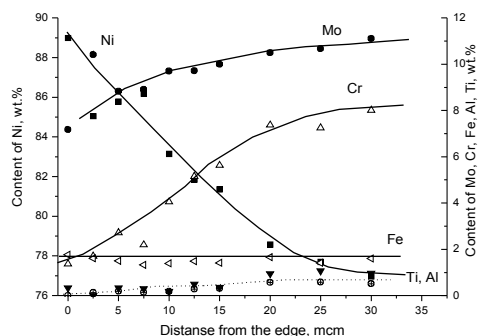


Fig. 8. Composition of the alloy after durable treatment in the melt along the cross-section of Fig. 7. The data obtained by X-ray microanalysis

It can be confirmed by comparing of the rate of diffusion with the observed corrosion current:

$$\frac{i}{nF} = D \frac{dC}{dx}, \quad (6)$$

where C is the concentration of oxidized species and i is mean corrosion current density. The derivative in the right of (6) can be estimated from the data of Fig. 7 as a slope of concentration profile, and average current from its time dependency. The calculations give $D = 1,5 \cdot 10^{-10} \text{ cm}^2/\text{s}$, which is consistent with common values for the diffusion in solids.

Thus, the dynamics of the system is determined by complicated set of processes including slow transport of the alloy's components from the bulk metal to the surface. Development of mathematic model of the system and its theoretical analysis is necessary for deeper insight.

Considering the shortcut current of the cell as an oxidation current of Hastelloy (reaction 2), one can calculate the weight loss of the sample from total charge consumed, which can be found as the integral of current-time dependencies. For the data of Fig. 6, such calculation gives $Q=339 \text{ mAh}$ and $\Delta m=320 \text{ mg}$ for the reaction of Cr oxidation. Such estimation is rough because other metals (Ti, Al) should also oxidize.

Additions of lanthanum fluoride to the electrolyte do not change the qualitative character of the process (Fig. 9).

This is expectable, because La metal is very chemically active and its fluoride could hardly ever be reduced thus affecting the processes in the cell.

The behavior of the cell is somewhat different in case when CC composite carbon material is used instead of

glassy carbon (Fig. 10). After 12 days of continuous work, the sign of electrodes changed and the metal electrode became positive.

Higher chemical activity and larger real surface of the CC material comparatively to GC is evidently the reason for this. The reduction of $Zr(IV)$ (1c) in this case is then faster and higher is the rate of accumulation of Zr intermediates in the melt. Thus, potential of C electrode moves far to the negative values and becomes eventually more negative than the Hastelloy.

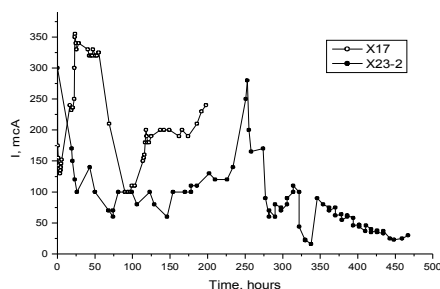


Fig. 9. Time dependencies of shortcut currents for the cells (-)X17/ZrF₄-NaF/C(+) and (-)X23-2/ZrF₄-NaF+6,7%LaF₃/C(+). The conditions are similar to that of Fig. 5

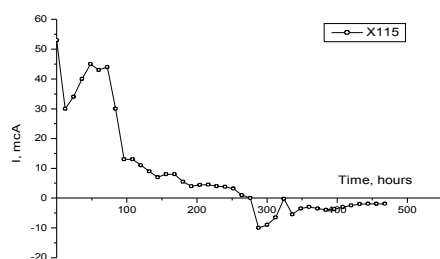


Fig. 10. Shortcut current of the cell X108/ZrF₄-NaF/C, where C - CC composite material

After the signs change, reduction reaction prevails at H electrode and corrosion process is suppressed.

The carbon electrode becomes an anode of the cell from the very beginning (the sign “-“) if Zr metal is added to the melt. Zirconium is deposited on the bottom of carbon crucible, which is also the C electrode of the cell. Being an active metal, it dissolves anodically:



Conjugated cathode reaction (1) proceeds in parallel. Hence, total process at C electrode is the dissolution of zirconium metal, which passes into the melt in form of intermediate valence species.

The process at H electrode is mainly the cathode reaction (1), the corrosion reaction can be neglected. Its rate is:

$$I_1^H = i_1^H S_H, \quad (8)$$

where i_1^H is current density, S_H is the surface area of H electrode. This I_1^H is the same shortcut current,

which we can measure. It is equal to algebraic sum of the currents related to the reactions (1) and (6) at C electrode.

Since the potential difference between the two electrodes in shortcut cell $\Delta\phi = IR$ is a few mV only (see above), we can consider the reaction (1) to proceed at the same potentials on both electrodes. Hence, the current density of this process at both electrodes should be practically the same:

$$i_1^H = i_1^C = i_1 \quad (9)$$

Then, following conclusion comes from the above: The H electrode serves as a probe for direct rate measurement of the reaction of Zr metal with the melt at its dissolution:

$$\frac{I_R}{S_C} = I \left(\frac{1}{S_H} + \frac{1}{S_C} \right) \quad (10)$$

or, taking into account that $S_c \gg S_x$,

$$I_R \approx \frac{I}{S_H} S_C \quad (11)$$

That is, measuring the shortcut current allows for direct determination of reaction rate of Zr metal with the melt according to the equation:



Figs. 11 and 12 present the data for two electrolytes, one of them containing additives of LaF_3 .

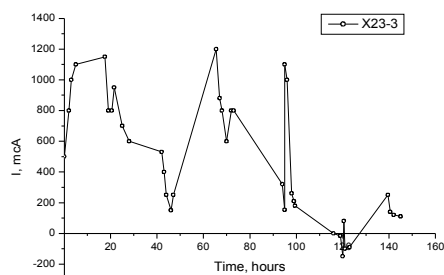


Fig. 11. Time dependence of shortcut current for the cell (-)C/ZrF₄ – NaF + Zr/X23(+). Zirconium content 3,5%, temperature 600°C, electrode surface areas as in Fig. 6

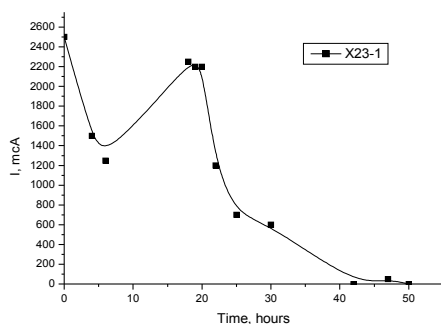


Fig. 12. Chortcut current for similar cell, Fig. 9, with 5% LaF_3 and 7,5% Zr

In spite of the oscillations, the current tends to decrease in both cases. Seemingly, the process (11) is over in 50 – 100 hours. The question upon the character of formed products is still open. Seems that they are hardly soluble in the melt and form solid deposits both on the metal (which is proved experimentally) and on the carbon surfaces.

CONCLUSIONS

As follows from the results of this work, measurements of shortcut currents of the cell Hastelloy/melt/carbon, together with analysis of polarization curves of separate electrodes, can be used as a method for investigation of the electrochemical reactions in Hastelloy – fluoride melt – carbon system. Following conclusions can be drawn:

- corrosion of Hastelloy enhances in the melt ZrF_4 – NaF (eut) if the alloy is in contact with carbon material;
- the shortcut current corresponds to the rate of corrosion, which can be used to estimate the depth of corrosion from these data;
- additions of lanthanum fluoride to zirconium fluoride – sodium fluoride melt does not significantly effect the corrosion processes;
- zirconium metal reacts with the melt. If it is present in the system, measurement of shortcut currents permits to study the rate of this reaction in a long-term process.

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КОРРОЗИОННЫЕ ПРОЦЕССЫ В РАСПЛАВЕ ФТОРИДОВ ЦИРКОНИЯ И НАТРИЯ. ИССЛЕДОВАНИЕ КОРОТКОЗАМКНУТОГО ЭЛЕМЕНТА C/(ZrF₄ – NaF)_{ЕВТ}/ХАСТЕЛЛОЙ

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Исследована временная зависимость параметров (ток, напряжение, внутреннее сопротивление) короткозамкнутого гальванического элемента хастеллой/углеродный материал в эвтектическом расплаве NaF-ZrF₄ при 600-650°C. Анализ этих данных, в совокупности с данными поляризационных измерений на отдельных электродах при разомкнутой цепи, показал, что ток короткого замыкания соответствует скорости коррозии сплава в контакте с углеродом при условии, если металлический Zr в системе отсутствует. В присутствии же Zr этот ток определяется скоростью взаимодействия циркония с расплавом (отнесенной к единице поверхности хастеллоя), что может быть использовано для исследования кинетики растворения циркония в расплаве. Установлено, что контакт сплава с углеродом усиливает коррозию как в чисто эвтектическом расплаве, так и с добавками LaF₃. Присутствие же металлического Zr подавляет коррозионный процесс.

КОРОЗИЙНІ ПРОЦЕСИ В РОЗПЛАВІ ФТОРИДІВ ЦИРКОНІЮ І НАТРІЮ. ДОСЛІДЖЕННЯ КОРОТКОЗАМКНЕНОГО ЕЛЕМЕНТА C/(ZRF₄ – NAF)_{ЕВТ}/ХАСТЕЛЛОЙ

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Вивчена зміна в часі параметрів (струм, напруга, внутрішній опір) короткозамкнутого гальванічного елемента хастеллой/вуглецевий матеріал в евтектичному розплаві NaF-ZrF₄ при 600-650°C. Аналіз цих даних в сукупності з даними поляризаційних вимірювань на окремих електродах при розімкнутому колі показав, що струм короткого замикання відповідає швидкості корозії сплаву в контакті з вуглецем при умові, якщо металічний Zr в системі відсутній. В присутності Zr цей струм визначається швидкістю взаємодії цирконію з розплавом (віднесеної до одиниці поверхні хастелою), що може бути використано для дослідження кінетики розчинення цирконію в розплаві. Встановлено, що контакт сплаву з вуглецем посилює корозію як в чисто евтектичному розплаві, так і з добавленням LaF₃. Присутність металічного Zr пригнічує корозійний процес.