Original Article

Al–Zr alloys synthesis: characterization of suitable multicomponent low-temperature melts

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A R T I C L E   I N F O

Article history:
Received 15 July 2019
Accepted 31 October 2019
Available online 15 November 2019

Keywords:
Al–Zr alloy
Electrical conductivity
Zirconia
Electrochemical synthesis
Melten cryolite salts
Advanced technology

A B S T R A C T

Al–Zr alloys as an advanced metal matrix composite material start to be attractive for various special applications. The electrochemical preparation of aluminium–zirconium alloy from cryolite melts seemed to be very perspective. Characterization of low-temperature sodium and potassium cryolite-based systems with the different additions of ZrO₂ and Al₂O₃ (both as an electrochemical active compounds) was realized. The electrical conductivity of NaF–AlF₃–Al₂O₃–ZrO₂ and KF–AlF₃–Al₂O₃–ZrO₂ systems as a function of the temperature was studied. The addition of AlF₃ varied from 33 mol% to 42 mol% in the sodium cryolite system and from 40.0 mol% to 45.5 mol% in the potassium cryolite system. Alumina and/or zirconia were added in amounts up to 1.2 mol% and 2 mol%, respectively (sodium system), and up to 2.8 mol% and 3 mol%, respectively (potassium system). The behavior of the electrical conductivity in the studied systems was described by the regression equations valid in a large temperature and concentration ranges.

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1. Introduction

The demand on metal matrix composites (MMC), especially the aluminium-based alloys is becoming stronger. The aluminium is a relatively low cost and easily fabricated, lightweight metal that can be heat treated to fairly strength level which makes it very attractive. The unique combinations of the properties of the aluminum and its alloys make aluminium one of the most versatile, economical, and attractive metallic materials for a broad range of applications as aerospace, automobile, electronics or different advanced technologies [1–6].

Zirconium represents one of the modifiers of the aluminum and its alloys. The binary Al–Zr phase diagram shows that the maximum solubility of zirconium in aluminum is about 0.234 wt% at the peritectic temperature 660 °C. The solubility of Zr in molten aluminum increases with increasing temperature [7]. The addition of Zr to the Al–Zr alloys in the amounts of 0.02–0.2 wt% increase the strength of alloy by almost three times, as well as ensuring the stability of properties when heated to up to 300 °C [8,9]. Zirconium added to Al-based alloys also improves fatigue corrosion cracking and natural aging resistance [10,11].

The existing methods of Al–Zr alloys preparation are not economic and do not result in the production of high-quality alloys. The dissolution of the metallic zirconium in the molten aluminum is a slow process [12]. The preparation of Al–Zr alloys using the direct melting of the pure metals (one of the most commonly used method) is very complicated due to the
large differences between the densities and melting points of both liquid metals [12]. Progressive methods of Al–Zr alloys preparation, such as mechanical alloying [13–15] or magnetron sputtering [16] were extensively studied in the last decades. A reduction in the cost of Al–Zr alloys can be achieved by using of zirconia (ZrO$_2$). Zirconium dioxide in the aluminum matrix ensures high fracture toughness, wear resistance, thermal shock resistance, mechanical strength, and better surface finish characteristic [17]. Some researchers have investigated the influence of alumina and/or zirconia in aluminum MMC [18,19]. Several methods of preparing Al–Zr alloys using ZrO$_2$ as cheaper and more available source of zirconium were described [20–23].

Synthesis of aluminum–zirconium master alloys via ZrO$_2$ in the molten cryolite-based melts seems to be very promising. The aluminum-thermal reduction in KF–AlF$_3$ and KF–NaF–AlF$_3$ melts with the addition of Al$_2$O$_3$ and ZrO$_2$ in the temperature range (600–900) °C was studied [22]. The dependence of the solubility of ZrO$_2$ in the investigated melts on alumina concentration was also defined. Filatov et al. [23] focused on the effects of KF–NaF–AlF$_3$ melt composition, ZrO$_2$ concentration and aluminothermic synthesis parameters on the conversion rate of zirconium into aluminum. It is important to study the physicochemical properties of different cryolite–zirconia molten systems due to the electrochemical preparation of Al–Zr alloys from molten cryolite-based melts. One of the key properties is the solubility of zirconia in the molten sodium, potassium and/or sodium–potassium cryolite melts. Bao et al. [24] described the solubility of ZrO$_2$ in the sodium cryolite based system with the molar ratio MR = 2.2 (molar ratio MR = n(NaF)/n(AlF$_3$) or n(KF)/n(AlF$_3$)) and with the addition of alumina and CaF$_2$ in temperature range 960–980 °C. The solubility of ZrO$_2$ in the studied cryolite-based melts increased significantly with increasing temperature and addition of CaF$_2$. The solubility of ZrO$_2$ in NaF–AlF$_3$–Al$_2$O$_3$–CaF$_2$ system with MR = 2.2 reaches the value about 5.5 wt%. Another key physicochemical property of the electrochemical preparation of Al–Zr alloys from the molten cryolite systems is the electrical conductivity of the melts. Bao et al. [25] investigated the electrical conductivity of the high-temperature sodium cryolite system with the molar ratio MR = 2.2–2.6 and the addition of CaF$_2$, Al$_2$O$_3$ and ZrO$_2$ up to 5 wt%. The temperature range was from 955 °C to 1000 °C. The electrical conductivity of the low-temperature cryolite melts (below 950 °C) were studied in paper [26]. The influence of the various content of ZrO$_2$ in NaF–AlF$_3$ (MR = 1.6–2.0) and KF–AlF$_3$ (MR = 1.2–1.5) systems was studied. The temperature range varied from 875 °C to 1045 °C in the sodium system and from 650 °C to 840 °C in the potassium system.

The paper deals with the mutual influence of the addition of ZrO$_2$ and Al$_2$O$_3$ on the electrical conductivity of the low-temperature cryolite-based melts. The added amounts of Al$_2$O$_3$ were in the range (0–4) wt % and ZrO$_2$ were in the range (0.0–5.2) wt %. The electrical conductivity was studied in the basic NaF–AlF$_3$ and KF–AlF$_3$ systems (with ZrO$_2$ and/or Al$_2$O$_3$) in the temperature range from 650 °C to 1020 °C (MR varied from 1.4 to 2.0 in the sodium system and from 1.2 to 1.5 in potassium system). The concentration and the temperature dependencies of the electrical conductivity of all studied systems were described by regression equations.

Fig. 1 – Nyquist plot of impedance measured for NaF–AlF$_3$–2%Al$_2$O$_3$–2%ZrO$_2$ with MR = 1.8 at different temperatures.

2. Material and methods

2.1. Chemicals

All chemicals were of the analytical grade. NaF (p.a., Merck), Al$_2$O$_3$ (99.5%, Sigma Aldrich), ZrO$_2$ (99%, Sigma Aldrich), and NaCl (p.a., CentralChem) were dried for 4 h at the temperature about 450 °C. KF (p.a., Merck) was dried in the vacuum dryer with phosphorus pentoxide for 4 days, and then for another 3 days without P$_2$O$_5$ at the temperature of 200 °C. AlF$_3$ (Sigma Aldrich) was purified by sublimation in a platinum crucible at the temperature of 1250 °C.

2.2. Experimental apparatus

The experimental apparatus and measuring process was described in details in the previous paper [26]. The graphite crucible containing the mixture of the chosen composition was placed in a vertical furnace with argon atmosphere (99.996%) and heated up to the required temperature. The temperature was measured with a calibrated thermocouple PtRh10-Pt (uncertainty within ±0.3 °C). The measuring electrode made of pyrolytic boron nitride tube and tungsten rod was immersed into the molten mixture. This tube-type conductivity cell has a constant distance between the electrodes. Solartron Impedance/Gain Phase Analyzer 1260 and a Solartron ECHI 1287 were used for measuring the cell impedance. AC-techniques with a sine wave signal and small amplitude in the high frequency range were used. The measured impedance plots (Nyquist plots, Fig. 1) were evaluated with the nonlinear regression analysis using the equivalent circuit method (Fig. 2). Intersection of the impedance curves with the x-axis represents the value of the electrolyte resistance (R$_{el}$) in the proposed equivalent circuits (uncertainty lower than 0.5%). The electrical conductivities were calculated from R$_{el}$ and from the conductivity cell constant. The cell constant was determined by calibration with sodium chloride using data on the electrical conductivity of molten NaCl [27].
2.3. Liquidus temperature

The liquidus temperatures of NaF–AlF₃ system were taken from the phase diagram [28]. The temperature decrease of the multicomponent systems measured was estimated from the phase diagrams of the quasi binary systems (Na₃AlF₆–Al₂O₃, Na₃AlF₆–ZrO₂) [29]. The phase diagram of KF–AlF₃ system can be found in papers [30–32]. The liquidus temperatures in the ternary systems (with the additions of alumina or zirconia) were published in [29]. The relevance of the temperature of primary crystallization (TPC) estimation was verified by the electrochemical measurements. It is not possible to measure the electrical conductivity even in a slightly heterogeneous system with the method used.

2.4. Conductivity model

Detailed description on the conductivity model can be found in our previous papers [33,34]. This chapter briefly summarizes the basic characteristic of our conductivity model. Temperature dependence of the electrical conductivity can be expressed as an integrated Arrhenius type equation (Eq. (1)). Parameters A and B are calculated from Eqs. (2) and (3) for as few parameters as possible or from Eqs. (4) and (5) if we take into account the dependence on composition. \( \kappa \) represent the electrical conductivity, \( T \) is temperature in K and \( x \) is the molar fraction of additives.

\[
\kappa = A \cdot \exp \left[ \frac{1}{B} \left( \frac{1}{T} \right) \right] \\
A = A_0 + A_1 \cdot x_{\text{AlF}_3} + A_2 \cdot x_{\text{Al}_2\text{O}_3} + A_3 \cdot x_{\text{ZrO}_2} \\
B = B_0 + B_1 \cdot x_{\text{AlF}_3} + B_2 \cdot x_{\text{Al}_2\text{O}_3} + B_3 \cdot x_{\text{ZrO}_2} \\
A = A_0 + A_1 x_{\text{AlF}_3} + A_2 x_{\text{Al}_2\text{O}_3} + A_3 x_{\text{ZrO}_2} + A_4 x_{\text{ZrF}_4} + A_5 x_{\text{ZrO}_2} \\
B = B_0 + B_1 x_{\text{AlF}_3} + B_2 x_{\text{Al}_2\text{O}_3} + B_3 x_{\text{ZrO}_2} + B_4 x_{\text{ZrF}_4} + B_5 x_{\text{ZrO}_2}
\]

3. Results and discussion

3.1. Sodium system

The sodium system was studied for four different MRs (from 2.0 to 1.4 with a step 0.2). Four different amounts of zirconia (1, 2, 3, and 4 wt%), respectively were added into the system NaF–AlF₃–Al₂O₃–ZrO₂ with alumina content of 2 wt%. The compositions of studied melts with the respective temperature ranges are shown in Table 1.

The electrical conductivity in the cryolite-based mixtures depends on the anion structure of the melt. The electrical conductivity of the sodium cryolite melts is mostly driven by mobile small Na⁺ cations. The addition of other compounds such as Al₂O₃, ZrO₂ or of higher amount of AlF₃ causes formation of larger ionic species [29,35]. These species do not support the ionic mobility of the melt; which causes lower electrical conductivity. Some large ion species will be generated after the addition of ZrO₂ [25].

\[
5\text{AlF}_3^3^- + 2\text{ZrO}_2 = 3\text{AlOF}_2^4^- + \text{ZrO}_2F_2^- + \text{ZrF}_4 + 2\text{AlF}_3
\]

\[
n\text{Zr}^{4+} + n\text{F}^- = [\text{ZrF}_n^{4-n}]^n
\]

The influence of these effects is visible in Figs. 3 and 4. The electrical conductivity of NaF–AlF₃–2%Al₂O₃–2%ZrO₂ melts decreases with decreasing molar ratio. The most significant drop in the electrical conductivity was observed for MR = 1.4 (temperature from 800°C to 880°C). The electrical conductivity of MR = 1.4 system is lower by ca 16% compared to MR = 1.6 system and more than 30% compared to MR = 2.0 system (Fig. 3).

![Fig. 3 – The electrical conductivity of NaF–AlF₃–Al₂O₃–ZrO₂ system as a function of temperature for different MRs. Contents of Al₂O₃ and ZrO₂: 2 wt%. Symbols: experimental data, full lines: data calculated from Eq. (8).](image-url)
The influence of different additions of \( \text{ZrO}_2 \) into NaF–AlF\(_3\)–Al\(_2\)O\(_3\) melts is shown in Fig. 4. The influence of single compounds (Al\(_2\)O\(_3\) and \( \text{ZrO}_2 \)) on the electrical conductivity in the low-temperature sodium cryolite melts was measured separately [26,34]. Alumina has the most significant negative effect on the electrical conductivity among the studied added compounds in these melts. The decrease in the electrical conductivity with the increasing alumina concentration strongly depends on MR. Drop in the electrical conductivity for MR = 2.0 was about 0.059 \( \Omega^{-1} \) cm\(^{-1} \) per 2 wt% of Al\(_2\)O\(_3\) and for MR = 1.4 it was about 0.105 \( \Omega^{-1} \) cm\(^{-1} \) per 2 wt% of Al\(_2\)O\(_3\) [34]. The addition of 2 wt% of zirconia into the NaF–AlF\(_3\) melts leads to the decrease in the electrical conductivity by average about 0.017 \( \Omega^{-1} \) cm\(^{-1} \) for MR = 2.0 [26] and about 0.056 \( \Omega^{-1} \) cm\(^{-1} \) for MR = 1.4. Simultaneous addition of both electrochemically active components into the basic system causes less pronounced decrease in the electrical conductivity as in the case of single additions. The drop in the electrical conductivity in NaF–AlF\(_3\)–2%Al\(_2\)O\(_3\)–2%ZrO\(_2\) system compared to binary NaF–AlF\(_3\) system at the same temperatures was about 0.064 \( \Omega^{-1} \) cm\(^{-1} \) for MR = 2.0 and 0.150 \( \Omega^{-1} \) cm\(^{-1} \) for MR = 1.4.

The electrical conductivity of the multicomponent sodium cryolite system containing alumina and/or zirconia can be calculated based on Eq. (1). The regression equation was constructed from the all available experimental data (binary, ternary and quaternary systems). The regression equations describing NaF–AlF\(_3\)–Al\(_2\)O\(_3\)–ZrO\(_2\) system were constructed by substituting the calculated parameters A and B in Eq. (1):

\[
\kappa (\Omega^{-1} \text{cm}^{-1}) = \frac{3.5207 - 3.7487x_{\text{AlF}_3} + x_{\text{ZrO}_2}(12.394 - 47.535x_{\text{AlF}_3})}{\exp \left[ (1098.8 + 1033.3x_{\text{AlF}_3} + 6186.8x_{\text{ZrO}_2} + 706.64x_{\text{Al}_2\text{O}_3}) \cdot \left( \frac{1}{1300} - \frac{1}{T} \right) \right]}
\]

where \( x_i \) is the mole fraction of additive i and \( T \) is a temperature in K. Coefficients in Eq. (8) are valid in the concentration range (33–42) mol mol\(^{-1} \) of AlF\(_3\) and in the temperature interval from TPC up to (80–100)°C of superheat. The concentrations of additives are in the range 0–1.2 mol% of Al\(_2\)O\(_3\) and 0–2 mol% of ZrO\(_2\), respectively. The standard deviation was found to be 0.0213 \( \Omega^{-1} \) cm\(^{-1} \).

3.2. Potassium system

The potassium system was studied for four different MRs (from 1.5 to 1.2 with a step 0.1). The alumina solubility in KF–AlF\(_3\) system is higher by ca 2 wt% than in the sodium one even at low temperatures [36]. Therefore, the alumina content in the potassium system was chosen to be 2 wt% and 4 wt%. Zirconia is also more soluble in the potassium system as in the sodium one [22]. Three different amounts of zirconia (1.7, 3.4, and 5.2 wt%) were added into NaF–AlF\(_3\)–Al\(_2\)O\(_3\)–ZrO\(_2\) system. The compositions of studied melts with the respective temperature ranges are shown in Table 2.

The potassium cryolite melts are completely ionized to K\(^+\), AlF\(_4^-\), AlF\(_3^-\) and AlF\(_6^{3-}\) [29,37]. Other possible reactions of AlF\(_6^{3-}\) anion depending on AlF\(_3\) are explained in previous work [37] in more details. The most mobile ions are K\(^+\) cations in this kind of melts. The differences in K\(^+\)/Na\(^+\) cation size causes the significant drop in the electrical conductivity of KF–AlF\(_3\) melts compared to NaF–AlF\(_3\) system at the same conditions [38].

The electrical conductivity of various compositions of KF–AlF\(_3\)–Al\(_2\)O\(_3\)–ZrO\(_2\) system decreases with decreasing temperature, similarly as in the sodium one (Fig. 5). However, the main difference between these two systems is the influence of the addition of aluminum fluoride. This addition slightly increases the value of the electrical conductivity in the potassium system at the same temperatures. The drop in the electrical conductivity between the binary KF–AlF\(_3\) system and the multicomponent one with the various additions of Al\(_2\)O\(_3\) and ZrO\(_2\) was negligible. Decrease in the electrical conductivity for addition of 1 wt% of Al\(_2\)O\(_3\) was in average by 0.0203 \( \Omega^{-1} \) cm\(^{-1} \) [37], and for 3.4 wt% of ZrO\(_2\) was about 0.025 \( \Omega^{-1} \) cm\(^{-1} \) [26]. Mutual influence of addition of both electrochemically active compounds to potassium melt shows less significant impact on the drop of the electrical conductivity as the sum of single additions. Decrease in the electrical conductivity in KF–AlF\(_3\)–2%Al\(_2\)O\(_3\)–3.4%ZrO\(_2\) melt (Fig. 5A) or in KF–AlF\(_3\)–4%Al\(_2\)O\(_3\)–3.4%ZrO\(_2\) melt (Fig. 5B) achieves on average the value 0.0527 \( \Omega^{-1} \) cm\(^{-1} \) and 0.0845 \( \Omega^{-1} \) cm\(^{-1} \), respectively.

Different additions of ZrO\(_2\) to the KF–AlF\(_3\)–Al\(_2\)O\(_3\) system with MR = 1.4 were also studied (Fig. 6). The alumina content was 2 wt% and/or 4 wt%; the zirconia content varied from 0 to 5.2 wt%. Increasing zirconia content in the melt causes more negative impact on the value of the electrical conductivity. The highest difference in the electrical conductivity between
Table 2 – The composition of the KF–AlF₃ electrolyte, the operating temperature ranges, and the additions of alumina and zirconia in weight and molar percent.

<table>
<thead>
<tr>
<th>MR</th>
<th>x(KF–AlF₃)/mol%</th>
<th>t/°C</th>
<th>x(Al₂O₃)/wt%</th>
<th>w(Al₂O₃)/mol%</th>
<th>x(ZrO₂)/wt%</th>
<th>w(ZrO₂)/mol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>60.0–40.0</td>
<td>795–836</td>
<td>2/4</td>
<td>1.38/2.78</td>
<td>3.4</td>
<td>1.96</td>
</tr>
<tr>
<td>1.4</td>
<td>58.0–42.0</td>
<td>722–805</td>
<td>2/4</td>
<td>1.37/2.76</td>
<td>3.4</td>
<td>1.94</td>
</tr>
<tr>
<td>1.3</td>
<td>56.5–43.5</td>
<td>661–741</td>
<td>2/4</td>
<td>1.36/2.74</td>
<td>1.7–5.2</td>
<td>0.96–2.97</td>
</tr>
<tr>
<td>1.2</td>
<td>54.5–45.5</td>
<td>654–736</td>
<td>2/4</td>
<td>1.35/2.72</td>
<td>3.4</td>
<td>1.92</td>
</tr>
</tbody>
</table>

Fig. 5 – The electrical conductivity of KF–AlF₃–Al₂O₃–ZrO₂ system as a function of temperature for different MR. (A) Contents of Al₂O₃ and ZrO₂ were 2 wt% and 3.4 wt%, respectively. (B) Contents of Al₂O₃ and ZrO₂ were 4 wt% and 3.4 wt%, respectively. Symbols: experimental data, full lines: data calculated from Eq. (9).

Fig. 6 – The electrical conductivity of KF–AlF₃–Al₂O₃–ZrO₂ system as a function of temperature for MR = 1.4 and different zirconia contents. (A) 2 wt% of alumina. (B) 4 wt% of alumina. Symbols: experimental data, full lines: data calculated from Eq. (9).

KF–AlF₃ and the multicomponent one (Fig. 6) was observed at 5.2 wt% of zirconia. The drop in the electrical conductivity was about 6.5% and 9.5% in KF–AlF₃–2%Al₂O₃–ZrO₂ and KF–AlF₃–4%Al₂O₃–ZrO₂ system, respectively.

The electrical conductivity of the multicomponent potassium system containing alumina and/or zirconia was calculated based on Eq. (1). The regression equation was constructed from all available experimental data. The regression equation describing KF–AlF₃–Al₂O₃–ZrO₂ system was constructed by substituting the fitted parameters A and B from Eqs. (2)–(5) to Eq. (1):

$$\kappa (\Omega^{-1} \text{cm}^{-1}) = (0.94153 + 1.1794x_{\text{AlF}_3} + x_{\text{ZrO}_2}(3.8872 - 14.463x_{\text{AlF}_3} - 2.3232x_{\text{Al}_2\text{O}_3}) \times \exp \left[ (936.97 + 17058x_{\text{AlF}_3} - 2694x_{\text{ZrO}_2} + 2444.8x_{\text{Al}_2\text{O}_3}) \cdot \left( 1 \frac{1}{1300} - \frac{1}{T} \right) \right]$$  (9)
where \( x_i \) is the mole fraction of the additive \( i \) and \( T \) is a temperature in K. The coefficients in Eq. (9) are valid for the concentration range (40–45.5) mol mol\(^{-1}\) of AlF\(_3\) and in the temperature range from TPC up to (80–100) °C of superheat. The concentrations of the additives were 0–2.8 mol\% of Al\(_2\)O\(_3\), and 0–5.2 mol\% of ZrO\(_2\). The standard deviation was found to be 0.0087 \( \Omega^{-1} \text{cm}^{-1} \).

4. Conclusions

The electrical conductivity of the low-temperature multi-component sodium and potassium cryolite systems was determined. Mutual influence of alumina and zirconia addition to the basic NaF–AlF\(_3\) system on the electrical conductivity causes less pronounced decline as a sum of the individual effects. The decrease in the electrical conductivity strongly depends on the aluminum fluoride content in the melt. The drop in the electrical conductivity in NaF–AlF\(_3\)–2%Al\(_2\)O\(_3\)–2%ZrO\(_2\) system compared to binary system at the same temperatures and conditions was about 0.064 \( \Omega^{-1} \text{cm}^{-1} \) for MR = 2.0 and about 0.150 \( \Omega^{-1} \text{cm}^{-1} \) for MR = 1.4, respectively.

Different contents of AlF\(_3\) in KF–AlF\(_3\)–Al\(_2\)O\(_3\)–ZrO\(_2\) system show negligible influence on the electrical conductivity when compared to the influence of the various additions of alumina and zirconia, which is in contrary to the sodium system. The mutual effect of additions of ZrO\(_2\) and Al\(_2\)O\(_3\) on the electrical conductivity is less significant as a sum of individual additions, similarly as in the sodium system. The decrease of electrical conductivity reached in average the value 0.0527 \( \Omega^{-1} \text{cm}^{-1} \) in KF–AlF\(_3\)–2%Al\(_2\)O\(_3\)–3.4%ZrO\(_2\) melt at all measured MRs and approximately 0.0845 \( \Omega^{-1} \text{cm}^{-1} \) in KF–AlF\(_3\)–4%Al\(_2\)O\(_3\)–3.4%ZrO\(_2\) system at all MRs.

The experimental results were evaluated by the non-linear regression analysis. The differences between the experimental and calculated values of the electrical conductivity were lower than 1.72% for NaF–AlF\(_3\)–Al\(_2\)O\(_3\)–ZrO\(_2\) system with the standard deviation 0.0213 \( \Omega^{-1} \text{cm}^{-1} \) and 0.64% for the KF–AlF\(_3\)–Al\(_2\)O\(_3\)–ZrO\(_2\) system with the standard deviation 0.0092 \( \Omega^{-1} \text{cm}^{-1} \).

Conflict of interest

The authors Emília Kubiňáková, Vladimír Danieliik, and Ján Hiveš declare no conflict of interest.

Acknowledgements

This publication is the result of the project implementation: Center for materials, layers and systems for applications and chemical processes under extreme conditions-Stage II, ITMS No.: 26240120021 supported by the Research & Development Operational Program funded by the ERDF. This work was supported also by the Ministry of Education, Science, Research and Sport of the Slovak Republic within the project VEGA 1/0792/17.

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