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Aluminium/zirconium alloys obtained by Al underpotential deposition onto Zr from low temperature AlCl₃+NaCl molten salts

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Abstract: Contrary to the widely accepted hypothesis that it is not possible, aluminium underpotential deposition (UPD) onto zirconium from a low temperature (200, 250 and 300 °C) equimolar chloroaluminate melt was recorded. Furthermore, it was shown that aluminium UPD facilitates alloy formation between the deposited aluminium monolayer and the zirconium substrate by interdiffusion. The aluminium/zirconium alloys formed at the temperatures substantially lower than those needed for thermal preparation of the same alloys were: Al₃Zr₂ and Al₃Zr. Experimental techniques used were linear sweep voltammetry, potential step, scanning electron microscope, energy dispersive spectroscopy and X-ray diffraction were used for characterization of obtained electrode surfaces.

Keywords: electrochemical metal deposition; chloroaluminate melt; solid state interdiffusion; intermetallics

INTRODUCTION

Developments of various technologies over the last few decades have resulted in an increase in demand for aluminium/transitional metal alloys. Among them, Al/Mn, Al/Ti, Al/V, Al/Cr, Al/Zr and others, show promise for industrial application.¹ Aluminium’s specific characteristics like corrosion resistivity, low toxicity, relatively low price, make it a very compelling choice as base or an alloying component for alloys.

Al/Zr alloys reach in zirconium are already used as getters for adsorption and extraction of gases in spaces under vacuum. One of most used among them is St.101, which consists of 84% Zr and 16% Al which within the working temperature range (200-450 °C) successfully absorbs all atmospheric gases.² Zr additi-

*To the memory of Professor Konstantin Popov who passed away in January 2019. This work is dedicated to the recognition of his outstanding contribution to the knowledge of electrochemical metal deposition.

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on also influences the electric conductivity of Al alloys\(^3\) as well as the tensile properties of some alloys at higher temperatures.\(^2\) 6061 T6 alloy (Al-Mn-Fe-Si) found application in production of professional bicycle frames, which when alloyed with Zr (less than 1 at.\%), saw a five-fold increase in fatigue resistance. Addition of Zr to alloys of AA3003 (Al-Mn-Fe-Si) type, has the same influence through segregation of small deposits made of Al\(_3\)Zr particles which influence alloy recrystallization which leads to increase of microhardness.\(^4,5\) New lithographic plates made of at least 99.5 at.\% Al, as usual, but with 0.02 – 0.2 at.\% Zr show four times greater effectiveness at working temperatures of 320 °C than the ones with no Zr present.

Electrodeposition as a method to obtain alloys has yielded good results. However, in the case of aluminium alloys with transition metals, one has to take into account the well-known fact that Al and many of the transition metals cannot be electrodeposited from aqueous solutions because hydrogen is generated before they are deposited. Therefore, a number of nonaqueous media including inorganic molten salts, aromatic hydrocarbons, etheric solvents and ionic liquids, have been studied as potential electrolytes. Chloroaluminate molten salts, based on AlCl\(_3\) mixed with an inorganic chloride salts such as NaCl (at \(\approx 170\) °C) or an organic chloride salt such as: 1-(1-butyl) pyridinium chloride or 1-ethyl-3methylimidazolium chloride (at close to room temperatures) were investigated as media for aluminium electrodeposition as well.\(^6,7\)

Electrodeposition of metals, in general, occasionally includes underpotential deposition of metals as well.\(^8\)–\(^10\) The phenomenon of underpotential deposition (UPD) was described as a deposition of a metal onto another metal at the potential more positive than the reversible potential of the depositing metal. The result, in principle, should be a monolayer of the depositing metal on top of another metal. In 1974, Gerischer, Kolb and Przasnyski\(^11\)–\(^13\) had put forward the hypothesis to explain the origins of UPD. They claimed that in order for an underpotential deposition to appear, for a pair made of any two metals, there should exist a work function difference between the substrate metal (\(\Phi_S\)) and the deposited metal (\(\Phi_D\)) and it has to be negative. Soon thereafter, the formation of aluminium alloys by interdiffusion between the underpotential atomic monolayer and the substrate became obvious in the examples observed in melts-electrolytes at elevated temperatures.\(^9,14–21\)

Published works on electrodeposition of Al/Zr alloys are rare. Kawase \textit{et al.} reported the electrodeposition of Al/Zr alloy films on a carbon-coated ceramic substrate from LiCl-KCl eutectic molten salts at 550 °C.\(^22\) Tsuda \textit{et al.} electrodeposited Al/Zr alloys on Cu wire from aluminium chloride+1-ethyl-3methylimidazolium chloride melt at 80 °C.\(^7\) There is also an example of Al/Zr alloy coatings electrodeposited on Cu from dimethylsulphone-based baths at 110 °C by Shiomi \textit{et al.}\(^23\) To the best of our knowledge, aluminium electrodeposition, especially
aluminium underpotential deposition onto zirconium and subsequent Al/Zr alloy formation from a chloroaluminate eutectic mixture has not been reported except in our initial announcement.\textsuperscript{24} The aim of the presented study was to investigate aluminium underpotential deposition onto zirconium from low temperature chloroaluminate molten salt and to establish if there was Al/Zr surface alloy formation.

**EXPERIMENTAL**

All electrochemical measurements were carried out in a three-electrode electrochemical cell, under an argon stream, controlled with Potentiostat/Galvanostat (Princeton Applied Research Model 273A Oak Ridge, TN, USA) equipped with appropriate software (Power Suite Software). Zirconium (Zr, 99.99 %; EMS Corporation, USA) wire and a planar plate were used as working electrodes. An aluminium (Al, 99.99 %, Alfa Products, Thiokol/Ventron division, USA) rod (0.3 cm diameter) and plate (7.5 cm\textsuperscript{2} surface area) were used as reference electrode and counter, respectively. Before each measurement, the electrodes were polished with 0.05 µm alumina powder (Merck, Germany) and washed with deionized water. Subsequently, zirconium electrodes were etched in a solution made of 50 vol% H\textsubscript{2}O + 1 vol% HF + 1 vol% HNO\textsubscript{3} and the aluminium electrodes in the solutions made of 50 vol% HF + 15 vol% H\textsubscript{2}O and conc. NH\textsubscript{4}OH + + 5 vol% H\textsubscript{2}O\textsubscript{2}. Finally, the electrodes were rinsed with deionized water, absolute ethyl alcohol, dried and mounted into the cell.

The procedures used for the electrolyte - chloroaluminate molten salt preparation and melt pre-electrolysis, were identical to those described in our previous work.\textsuperscript{15} Linear sweep voltammetry (LSV) experiments were carried out in a potential range starting from an initial potential, \(E_i\) (slightly negative to the zirconium reversible potential) to a final negative potential, \(E_f\) (15-100 mV negative to the aluminium reversible potential) followed by a return scan. Voltammograms performed in the aluminium underpotential deposition range included similar potential range scanned, except that the scan direction was changed when the potential reached \(E_f = 0.010\) to 0.050 V, positive to the aluminium reversible potential, and sometimes this \(E_f\) potential was held for \(t_d = 1, 5\) and 10 minutes. After holding, the potential was swept back to the initial potential, \(E_i\).

Electrochemical potentiostatic deposition was carried out at a constant aluminium underpotential (0.010 V) or some chosen overpotential values (-0.010 V) at three different temperatures (200, 250 and 300 °C), for 2 hours, whereupon the working electrode was retrieved from the cell under potential in order to preserve deposited material or possible alloys formed. The working electrode was then washed with absolute ethyl alcohol (Zorka-Pharma, Šabac, Serbia) to remove the melt residues, and dried in a desiccator furnished with silica gel. All the reported potentials of working electrodes in this work were measured relative to the equilibrium potential of aluminium reference electrode in the melt used under given conditions.

The morphology, microstructure and composition of the deposits were analysed by scanning electronic microscope (SEM: JEOL, model JSM-5800, Tokyo, Japan), energy dispersive spectroscopy EDS and EDX mapping (Oxford INCA 3.2, Abingdon, U.K.). After the potentiostatic electrodeposition, the Zr working electrode was examined by X-ray diffraction (XRD) on a Philips PW 1050 powder diffractometer at room temperature with Ni filtered CuK\textsubscript{α} radiation (\(λ = 1.54178\) Å), scintillation detector within 15–75° 2\(θ\) range in steps of 0.05°, and scanning time of 5 s per step. The diffractograms identifying phases formed during the deposition were compared to the recorded diffraction peaks with the Joint Committee on Powder Diffraction Standards (JCPDS) database.
RESULTS AND DISCUSSION

Fig. 1 exhibits potentiodynamic polarization curves \((v = 1 \text{ mV s}^{-1})\) obtained on a zirconium electrode from equimolar \(\text{AlCl}_3+\text{NaCl}\) molten salt electrolyte at different temperatures used. There are at least two apparent reversible potentials positive to the aluminium reversible potential recorded at each temperature applied. Those recorded at the potentials close to the value of 0.000 V should reflect the reversible aluminium potential in the electrolyte used. However, there is at least one more reversible potential, positive to the aluminium reversible potential, which should be attributed to some phase other than metal Al, being formed during overpotential and underpotential regimes applied.

Fig. 1. Potentiodynamic polarization curves obtained on a zirconium electrode in equimolar \(\text{AlCl}_3+\text{NaCl}\) molten salt at different temperatures: a) 200 °C; b) 250 °C and c) 300 °C.

Typical voltammograms obtained from a Zr working electrode in the used melt applying different sweep rates at different temperatures in the aluminium underpotential range are shown in Fig. 2. They show cathodic current waves with small amplitudes as well as equally small corresponding anodic current counterparts.
Fig. 2. Voltammograms recorded on zirconium electrode applying different sweep rates in equimolar AlCl₃+NaCl molten salt at different temperature: a) 200 °C; b) 250 °C and c) 300 °C.

Fig. 3. Voltammograms recorded on Zr electrode in used melt when cathodic end potential $E_t$ = 0.010V was held for different period of time; $\nu$ = 10 mV s⁻¹, a) $T$ = 200 °C; b) $T$ = 250 °C.
These current waves had not pronounced profiles and sharp peaks. However, a continuous increase of the reduction current, as the potential was changed from 0.150 V towards 0.000 V, was observed. The same was the case with the anodic current waves when the change in direction of the potential was made. The charge encompassed by the cathodic current waves and corresponding anodic current waves was similar in value and greater than the charge needed for the electrodeposition of one closest packed aluminium monolayer. Increasing the working temperature, as well as the sweep rates, induces higher current densities but does not significantly change the profiles of the curves.

Characteristic results were recorded when the LSV cycle was interrupted for controlled period of time at the working electrode “holding potential” - \( E_f \) (the most negative potential in the cycle) Fig. 3. The current at the “holding potential”, although in the Al underpotential region, increased slightly with an increase in holding time, and so did the subsequent corresponding dissolution charges. An increase in the working temperature, all other conditions kept constant, led to an increase of the charge limited by the dissolution current. The anodic current waves became more pronounced and their peaks appeared at the potentials similar to those indicated by the polarization curves seen in Fig. 1. In any case, the increase of the cathodic and corresponding anodic charges suggests an increase in the underpotentially deposited and dissolved aluminium.

Appearance of such reduction and oxidation current waves, which do not show pronounced amplitudes in voltammograms recorded in the underpotential range, are characteristic of metal underpotential deposition and dissolution in some other cases.\(^ {18,19} \) Those cases suggested that such voltammograms represent underpotential deposition of aluminium onto Zn and Cd substrate even though, according to Gerischer \( \text{et al.} \),\(^ {11-13} \) underpotential deposition should not occur. Namely, the half of the difference of electron functions between Al and Zn, and Al and Cd is negative or very close to zero and as a result, there should not be a driving force for Al underpotential deposition onto Zn or Cd substrates. However, there was aluminium underpotential deposition in those cases and it was always accompanied by alloy formation between deposited Al and Cd or Zn substrate. It appears that the Al/Zr pair in the same electrolyte and under the same temperatures used behaves very similarly to Al on Cd and Al on Zn pairs, \( i.e. \) there seems to be an Al underpotential deposition onto the Zr surface, as well as Al/Zr alloy formation.

Change of the working electrode “open circuit potential” with time, after being held for 60 minutes at the Al underpotential of 0.020 V, is presented in Fig. 4. at all the three deposition temperatures applied (200, 250 and 300 °C). At least one plateau was observed at a potential different from the one reflecting aluminium or Zr reversible potentials in the system used. The values of these plateaux potentials are close to the values of the reversible potentials in the
aluminium underpotential region recorded in Fig. 1, a, b and c. By definition, these potentials define a phase on the electrode surface in equilibrium with its ions in the electrolyte. Since the plateaux potentials are substantially more positive than the aluminium reversible potential in the system observed, they should not reflect bulk aluminium on the surface of the Zr working electrode in equilibrium with aluminium ions in the electrolyte. However, these potentials can be reversible potentials of the zirconium / aluminium surface alloys made by aluminium underpotential deposition onto zirconium and subsequent interdiffusion with the substrate. This approach is supported by LSV results, Figs. 2 and 3, and agrees with the findings reported elsewhere.18,19

The results of LSV experiments with the cathodic end potential $E_f$ being led into aluminium overpotential region using the same sweep rate at different temperatures are presented in Fig. 5.

Two features were observed: i) there was a current increase announcing Al bulk deposition at the potentials cathodic to $\approx -0.030$ V and anodic counterpart at the potentials anodic to $\approx 0.000$ V reflecting dissolution of the deposited bulk Al; ii) at 250 °C there was a hint of an anodic current increase at $\approx 0.175$ V, and at 300 °C a visible anodic current wave formed with the peak at $\approx 0.175$ V. This group of second anodic current waves appeared at the anodic potentials very close to those seen in Figs. 2-4, and most probably represent dissolution of the surface Zr/Al alloys formed by aluminium underpotential deposition and interdiffusion with the zirconium substrate.
These assumptions were supported by voltammograms obtained when negative end potential of the cycle was held for some time in the aluminium overpotential range and then return back to the starting potential of the cycle. Resulting large anodic dissolution current waves, whose amplitude and peak number increases with increased holding time of the chosen cathodic overpotential, were recorded, Fig. 6. The charge under the anodic current waves indicates dissolution of aluminium previously deposited, but the appearance of a multipeak structure obtained with increased holding time suggests additional phase(s) being formed. The peak potential of the second anodic peak, $\approx 0.175 \text{ V}$, agrees well with the anodic peak potential values seen in voltammograms Figs. 2, 3 and 5, and plateaux potential values recorded by polarization curve and open circuit measurements, Figs. 1 and 4. It should be concluded that part of the deposited aluminium enters the substrate, forms an alloy with the substrate, which is then dissolved at anodic potentials close to $\approx 0.175 \text{ V}$. The finding that this alloy dissolution peak appears at the same potentials as a result of similar experiments, Figs. 2 - 4, in the underpotential range, suggests Al/Zr alloy formation by Al underpotential deposition onto Zr substrate in the system investigated.

SEM, EDS and EDX analyses of the working electrode surface exposed for some time to aluminium underpotentials, provided additional data on aluminium being underpotentially deposited onto zirconium substrate in the system investigated, Fig. 7. Particularly convincing were EDS and EDX analysis results which not only register the presence of aluminium on the zirconium substrate after underpotential deposition but give comparative maps of aluminium and zirconium distribution in the working electrode surface. The white areas in the EDX maps from Fig. 7 indicate positions and distribution of the elements: 7c) zirconium, 7d) aluminium and 7e) oxygen present in the sample surface. These results conclusively confirm aluminium underpotential deposition onto zirconium proposed on the grounds of the experimental results presented in Figs. 2-6.
Examples of XRD diffraction patterns of zirconium substrates exposed for some time to aluminium underpotential (0.010 V) at three chosen temperatures are exhibited in Fig. 8. Each of them indicates presence of at least two Al/Zr alloys. Difference introduced between XRD spectra for substrate samples obtained at different working temperatures is shown in different number of Al/Zr alloys being formed as a result of aluminium underpotential deposition in the system investigated. There was no bulk aluminium being recorded. Alloy Al$_3$Zr was present in the substrate surface irrespective of the working temperature after aluminium underpotential deposition. The same alloy was the only alloy made by overpotential Al deposition, see Fig. 9. This implies that a significant supply of aluminium to the substrate surface, compared to underpotential deposition, continue to favour formation of what seems to be an alloy with the lowest energy of formation for the governing conditions in all the systems investigated.

Final evidence of aluminium underpotential deposition and alloy formation with zirconium substrate in the chosen system under chosen temperatures and other conditions were provided by the XRD analysis of the working electrodes after prolonged time spent under investigated aluminium underpotential, Fig. 8.
Fig. 8. XRD spectra of zirconium electrode surface after aluminium underpotential was applied:

$E = 0.010 \text{ V, for 2 hours, at } 200 \degree \text{C;}\ (\bullet) – \text{Al}_3\text{Zr}$

$E = 0.010 \text{ V, for 2 hours, at } 250 \degree \text{C;}\ (\bullet) – \text{Al}_3\text{Zr}^2\ (\ast) – \text{Al}_3\text{Zr}$

$E = 0.010 \text{ V, for 2 hours, at } 300 \degree \text{C;}\ (\bullet) – \text{Al}_3\text{Zr}^2\ (\ast) – \text{Al}_3\text{Zr}$

Formation of the first aluminium monolayer onto zirconium surface is followed by aluminium atoms diffusion into the substrate, the alloying process being continuously supplied with material by newly underpotentially deposited aluminium.

The results obtained in our investigation of underpotential aluminium electrodeposition onto zirconium from equimolar AlCl$_3$+NaCl melt at 200, 250 and 300 $\degree$C can nominate the formation of the following Al/Zr alloys:

- orthorhombic $\text{Al}_3\text{Zr}_2$, most intensive $2\theta$ values: 32.91°, 34.68°, 37.33°, 54.04°, 54.28°, 67.15°, [JCPDS No. 00-048-1383];
- tetragonal $\text{Al}_3\text{Zr}$, most intensive $2\theta$ values: 27.35°, 38.08°, 53.95°, 63.34°, 65.86°, 73.79°, 78.82°, [JCPDS No. 00-048-1385].

In discussing the possibility of Al/Zr alloy formation, one should bear in mind that among all of binary phase diagrams of aluminium with transition
metals, the Al-Zr diagram is one of the most complex.\textsuperscript{25,26} It consists of ten recognized compounds of different concentrations, each of which appears in a narrow concentration band (most often in the order of 1 at.%). Two of the phases (namely Zr$_5$Al$_3$ and Zr$_5$Al$_4$) are high temperature phases while the rest of the phases decompose and transform into other phases at higher temperatures. Most of the phases appear in hexagonal, orthorhombic, tetragonal and cubic structures and four of them appear in new prototype forms. Maximum solubility of aluminium in zirconium is 26 at.% at 1350 °C.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure9.png}
\caption{a) SEM photo of Zr electrode after 2 hours of Al potentiostatic deposition, $E_\text{a} = -0.010$ V, at 250 °C, magnification 100x; b) EDS analysis of the sample from a); c) XRD analysis: ● – Al$_3$Zr, ○ – Al.}
\end{figure}

It should be noted that a detailed review of the available literature did not provide us with reports on electrodeposition of aluminium onto zirconium from inorganic melts or ionic solutions either by underpotential or overpotential electrodeposition to compare our results with.
Meanwhile, last twenty years have seen several published works\textsuperscript{7,23,27} on the subject of electrolytical co-deposition of zirconium and aluminium from ionic solutions. In one of those papers\textsuperscript{7}, the authors elaborate on the dependence of the structure of the Al/Zr alloy deposited on chemical composition and temperature, and conclude that zirconium practically does not dissolve in fcc aluminium at room temperature. However, they found that metastable solid-state Al/Zr solutions show good thermal stability up to 400-450 °C. They explain that thermal decomposition of the saturated solid-state solution leads to nucleation of a metastable Al\textsubscript{3}Zr phase ordered into cubic Li\textsubscript{2} structure or to an equilibrated Al\textsubscript{3}Zr phase of tetragonal structure. Alloys with higher Zr content (up to 16.6 at.\%) should be entirely amorphous. Such two-phase regions are common among alloys obtained by co-deposition of aluminium with transition metals when concentration of the transition metal exceeds the saturation limit of the solid solution fcc structure in Al.

However, there is literature that reports on developments in physical manufacturing methods designed around the intimate contact of aluminium and zirconium thin layers, which to some extent resemble the interface studied in our work. There are examples where thin films of aluminium and zirconium, made by vacuum vapour deposition brought into contact at temperature between 553 and 640 °C, show alloy formation by interdiffusion.\textsuperscript{28,29} In such cases, only one intermediate phase was formed, namely Al\textsubscript{3}Zr. Authors proposed a sequence of events in the diffusion zone of the process leading to formation of said alloy:

a) Saturation of the initial solution with atoms of the solute,

b) Nucleation of the intermediate phase (Al\textsubscript{3}Zr), and

c) Growth of the newly formed phase.

At 600 °C, the solubility of Zr in Al is only 0.07 at.\% and of Al into Zr is 1.2 at.\%, so it should be expected that initial solid solution will be saturated first with aluminium.

The ease with which Al\textsubscript{3}Zr phase nucleation proceeds next to the aluminium surface can be explained by the structure of its lattice. Aluminium crystallizes as fcc lattice with first neighbour atomic distance of 2.86 Å. Al\textsubscript{3}Zr is body centered tetragonal lattice of DO\textsubscript{3} type and it can be easily considered as a slightly deformed modification of an fcc structure. In the Al\textsubscript{3}Zr structure, the Al-Al distance is 2.80 and 2.85 Å, which approaches the value of pure Al. It is obvious that Zr atoms orderly incorporation and positioning into the Al atom matrix leads to the formation of Al\textsubscript{3}Zr without significant strain energy.

High formation rate of Al\textsubscript{3}Zr compared to other phases is most probably the result of relatively large diffusion coefficients of Zr and Al in that phase. This suggests that concentration gradients are being formed through the defective lattice as a result of increased concentration of vacancies (positions not occupied by Al atoms in Al\textsubscript{3}Zr lattice). Each Al atom has eight Al and four Zr positions in
its coordination shell. At the same time, a Zr atom is completely surrounded only by Al positions. As a consequence, free Al position, which are in principle available to both Al and Zr atoms, will be more probably exchanged with an Al atom then with a Zr atom because the latter has to overcome a lattice order barrier in addition to the normal barrier needed to attain Al position. That is why the Zr diffusion coefficient through Al₃Zr phase is smaller than for Al.

The work that elaborates on mechanical Al/Zr alloying of two metal powders at room temperature agree with the above approach to zirconium being alloyed by diffusion of aluminium. During mechanical mixing (a mill with balls) of the Al and Zr powders, Zr grains become covered with an Al layer. Due to further friction, the Al layer dissolves and incorporates into the Zr structure by diffusion because of high negative enthalpy of mixing between Al and Zr. This leads to the formation of the Al concentration profile in Zr and to appropriate change of lattice parameters followed by a metastable disordered solid state solution. When Al concentration in Zr increases over 15 at.% (up to 40 at.% Al), hexagonal Zr structure becomes unstable and transforms into a glassy structure (amorphous phase of Zr₃Al). Above 50 at.% Al, a metastable face centred cubic lattice of ZrAl phase is formed.

In another work, the authors pressed nanocrystalline powders of Al and Zr at 76 to 100 °C and analysed the obtained Al/Zr alloy at room temperature. They found that even in the alloy made of 5-35 mass.% Zr, metastable cubic Al₃Zr L1₂ phase was observed, which appears in processes of abrupt solidification. This was contrary to the Al-Zr phase diagram which proposes coexistence of Al with changing quantities of ZrAl₃ of DO₂₃ phase. The assumption was that nucleation of simple L1₂ cell requires less energy than the bigger and more complex DO₂₃ structure. Smaller particles are more reactive and prone to higher diffusion rates, which reduces the nucleation barrier of the L1₂ phase.

Recently, a number of reports appeared which analyse formation of alloys by interdiffusion between zirconium and aluminium thin films, deposited onto silicon or graphite by magnetron spattering. These films have been heated at temperatures from 100 to 700 °C for one hour. It was established that interdiffusion between the films starts above 200 °C. The first visible changes in the structure of the multilayer system appeared at 250 °C followed by an increase in the interdiffusion rate and initiation of Zr and Al layers mixing into an amorphous alloy. At 290 °C, the interface consists of an amorphous Zr/Al alloy and a cubic Al₃Zr alloy. Above 295 and 298 °C, the interface phase alloys transform completely into a polycrystalline mixture of hexagonal close packed ZrAl₂ and cubic Al₃Zr.
CONCLUSION

Half of the difference between work functions of zirconium and aluminium is small and negative, therefore according to Gerischer-Kolb hypothesis\textsuperscript{9-11} there should not be underpotential deposition of aluminium onto zirconium.

However, our experiments in aluminium deposition onto zirconium from equimolar chloroaaluminate melts at potentials positive to aluminium reversible potential performed at 200, 250 and 300 °C revealed underpotential deposition of aluminium resulting in Al/Zr surface alloys formation. Alloys recorded were: Al\textsubscript{3}Zr\textsubscript{2} and Al\textsubscript{3}Zr.

The alloys were formed at temperatures several hundred degrees lower than the temperatures needed for the production of the same alloys by thermal processes.

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