



# ELECTROCHEMICAL SYNTHESIS OF TERNARY METAL CONTAINING COMPOSITE MATERIALS

**Nodar Gasviani<sup>[a]</sup>, Gulnara Kipiani<sup>[a]</sup>, Raul Kokilashvili<sup>[b]</sup>, Nino Skhiladze<sup>[a]</sup> and Grigol Imnadze<sup>[a]</sup>**

**Keywords:** electrochemical synthesis; composite materials; potentiostat electrolysis; halide melts.

The peculiarities of electrochemical preparation of composite materials (intermetallides, polymetallic powders: CoTaMo, CoNbMo, YMnMn, YAl) from various compounds (CoF<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, YF<sub>3</sub>, Na<sub>2</sub>MoO<sub>4</sub>, MnCl<sub>2</sub>, AlF<sub>3</sub>, Na<sub>3</sub>AlF<sub>6</sub>) against the background of halide metals: KCl, K, Na/Cl, K/Cl, F were studied. X-ray phase and chemical analyses of obtained materials were carried out.

\* Corresponding Authors

Fax: +995 599 14 39 50

E-Mail: [nodargasviani@mail.ru](mailto:nodargasviani@mail.ru)

- [a] R. Agladze Institute of Inorganic Chemistry and Electrochemistry of Ivane Javakhishvili Tbilisi State University, Georgia, Tbilisi, Mindeli str. 11, 0186
- [b] Department of Environmental Engineering and Ecology of Georgian Technical University, Georgia, Tbilisi, Kostava str. 77, 0171

## INTRODUCTION

The rapid technical growth of technological processes requests preparation of new composite materials (intermetallics) which operates at high temperatures and resist towards aggressive compounds, irradiation, and other harmful effects. These kinds of composites can be prepared in various ways, e.g. with electrochemical synthesis from compounds containing Al, Mn, high-melting and rare metals (Y, Ti, Zr, Hf, V, Nb, Ta, Mo, W)<sup>1-2</sup> or with high temperature (873K to 1173 K) diffusion (surface) alloying of base metals when the properties of the base metal (steel) is mainly determined by the surface composition instead of the volumetric one. Plasma chemical deposition, high-temperature self-propagating, and other methods have already been used to impart the useful properties to base metals and to save the scarce, expensive alloying metals.<sup>3</sup>

The composites (intermetallides, polymetallic powders) are characterized by good corrosion-, wear- and heat resistance and their properties in the most cases present the combination of the properties of the constituents. The exact prediction of the mentioned properties, however, is not possible. Except for the electrochemical synthesis, these methods require high temperature (1773-3773 K), while the electrochemical ways can be done at relatively lower temperatures (873-1173 K) with high variability of reaction conditions in melts with simultaneous deposition of metals at the cathode as a result of interactions at atomic levels.<sup>4</sup> It should be noted that the synthesis of two or three component materials may be carried out in thermodynamics (the difference between the potentials of electrochemical reduction of the components does not exceed 0.2 V, and the alloy composition is independent of current density) or kinetics (potentials difference exceeds 0.2 V, the alloy composition is independent of the potentials difference) controlled.

Due to their unique properties, tantalum and niobium and the composite materials containing these elements has high importance.<sup>4-6</sup> To prepare this type of composites, a thermodynamically controlled system is used by addition of oxygen-ion scavengers (Ba<sup>2+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, PO<sub>4</sub><sup>3-</sup>, etc.) to reach a quasi-equilibrium at the cathode environment.<sup>5</sup> To co-deposit of Ta, Nb, Mo, and Co from KCl-NaCl melt in the presence of various depolarizers are discussed.

## EXPERIMENTAL

All the compounds used were "chemically pure." They were preliminary dehydrated and melted.

Voltammetric experiments were carried out in a three – electrode electrochemical cell where glass-graphite was used as an anode and also as melt container. Platinum was used as the cathode and also as the reference electrode. Voltammograms (IV) were recorded in various background melts, e.g. KCl, K, Na/Cl, K/Cl, F in the temperature range from 973 to 1173 K by the use of potentiostat PI-50-1.

Electrolysis experiments were performed in a potentiostatic system in the potential range of -1.1÷-1.7 V at various concentrations of the depolarizers. The products obtained were analyzed by the methods of X-ray phase and chemical analyses.

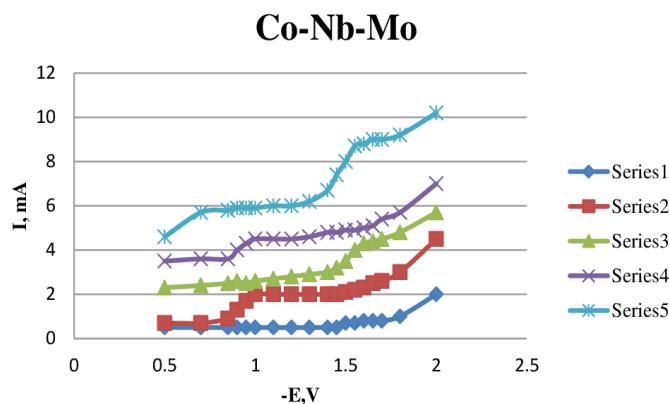
## RESULTS AND DISCUSSION

### Electrochemical synthesis of NbC-Mo and TaCoMo powders

The I-V characteristics of KCl-NaCl (1:1, wt/wt.) melt, together with the curves of the starting materials (CoF<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, and Na<sub>2</sub>MoO<sub>4</sub>, curves 2, 3 and 4, respectively) and the curve of the mixture containing all of the components are presented in the Fig.1. The reductions of Co, Nb and Mo compounds can be observed. It is evident that the differences between the potentials of the electroreductions are more than 0.2 V.

The voltammogram (curve 5) taken at the existence of all three starting compounds in the melt shows existence a single wave at  $-1.3 \pm -1.6$  V. The product formed during the potentiostat electrolysis at  $-1.6$  V was a polymetallic powder which X-ray phase analysis showed the peaks characteristic for Co, Nb, and Mo.

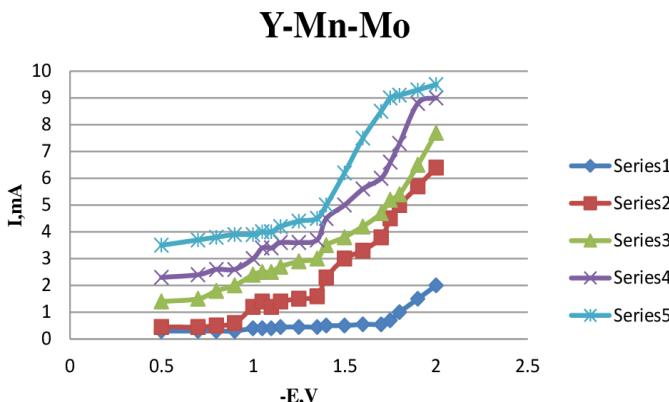
The similar picture could be observed in the case of replacement of  $\text{Nb}_2\text{O}_5$  by  $\text{Ta}_2\text{O}_5$  when a polymetallic powder containing metallic Co, Ta, and Mo was formed.



**Figure 1.** Voltammograms of the melt  $\text{Na},\text{K}/\text{Cl}(\text{F})$  containing  $\text{CoF}_2$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{Na}_2\text{MoO}_4$ , 1 – Base melt:  $\text{NaCl}-\text{KCl}$ ; 2 – Base melt +  $\text{CoF}_2$  ( $4 \cdot 10^{-5}$  mol  $\text{cm}^{-3}$ ); 3 – Base melt +  $\text{Nb}_2\text{O}_5$  ( $3.5 \cdot 10^{-5}$  mol  $\text{cm}^{-3}$ ); 4 - Base melt +  $\text{Na}_2\text{MoO}_4$  ( $4 \cdot 10^{-5}$  mol  $\text{cm}^{-3}$ ); 5 - Base melt +  $\text{CoF}_2$  ( $4 \cdot 10^{-5}$  mol  $\text{cm}^{-3}$ ) +  $\text{Nb}_2\text{O}_5$  ( $3.5 \cdot 10^{-5}$  mol  $\text{cm}^{-3}$ ) +  $\text{Na}_2\text{MoO}_4$  ( $4 \cdot 10^{-5}$  mol  $\text{cm}^{-3}$ ); cathode–platinum; reference electrode–platinum. Polarization rate  $0.1 \text{ V} \cdot \text{sec}^{-1}$ ,  $T=1023 \text{ K}$ .

#### Electrochemical synthesis of intermetallic – $\text{YMoMn}$

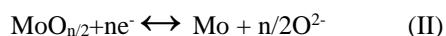
The voltammograms of  $\text{YF}_3$ ,  $\text{MnCl}_2$  and  $\text{Na}_2\text{MoO}_4$  and the eutectic  $\text{KCl}-\text{NaCl}$  melt contains these together are shown in Figure 2. Addition of depolarizer  $\text{MnCl}_2$  to eutectic melt  $\text{K}, \text{Na}/\text{Cl}$  at  $973 \text{ K}$  results appearance of three waves at  $-0.6 \pm -0.7$  V,  $-0.7 \pm -1.0$  V and  $-1.1 \pm -1.3$  V (Curve 2)



**Figure 2.** Voltammograms of the eutectic  $\text{KCl}-\text{NaCl}$  melt and  $\text{YF}_3$ ,  $\text{MnCl}_2$  and  $\text{Na}_2\text{MoO}_4$ , and mixtures of them. 1 – Base melt (eutectic); 2 – Base melt +  $\text{MnCl}_2$  ( $1 \cdot 10^{-4}$  mol $\cdot\text{cm}^{-3}$ ); 3- Base melt +  $\text{MnCl}_2$  ( $1 \cdot 10^{-4}$  mol $\cdot\text{cm}^{-3}$ ) +  $\text{YF}_3$  ( $1 \cdot 10^{-4}$  mol $\cdot\text{cm}^{-3}$ ); 4 - Base melt +  $\text{MnCl}_2$  ( $1 \cdot 10^{-4}$  mol $\cdot\text{cm}^{-3}$ ) +  $\text{YF}_3$  ( $1 \cdot 10^{-4}$  mol $\cdot\text{cm}^{-3}$ ) +  $\text{Na}_2\text{MoO}_4$  ( $1 \cdot 10^{-4}$  mol $\cdot\text{cm}^{-3}$ ); 5 - Base melt +  $\text{MnCl}_2$  ( $1 \cdot 10^{-4}$  mol $\cdot\text{cm}^{-3}$ ) +  $\text{YF}_3$  ( $1 \cdot 10^{-4}$  mol $\cdot\text{cm}^{-3}$ ) +  $\text{Na}_2\text{MoO}_4$  ( $6 \cdot 10^{-4}$  mol $\cdot\text{cm}^{-3}$ ). Cathode–platinum; reference electrode–platinum. Polarization rate  $0.1 \text{ V} \cdot \text{s}^{-1}$ ,  $T=973 \text{ K}$ .

Due to the presence of aerial oxygen,  $\text{Mn}(\text{II})$  was transformed into  $\text{Mn}(\text{VI})$  which reduces in three stages into metallic manganese ( $\text{Mn}^{\text{VI}}-\text{Mn}^{\text{IV}}$ ,  $\text{Mn}^{\text{IV}}-\text{Mn}^{\text{II}}$  and  $\text{Mn}^{\text{II}}-\text{Mn}^{\text{0}}$ ). At the potential, appropriate to limiting currents of the first and second waves there was no deposit formation on the cathode, while at the potential  $-1.3$  V, which belong to the to limiting current of the third wave, metallic manganese was obtained.

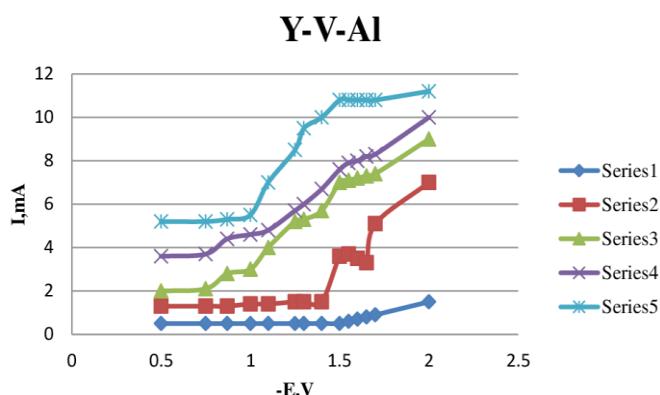
One wave could be seen at relatively high concentrations of the molybdate in the potential range  $-0.75 \pm -1.75$  V on the voltammogram of the melt:  $\text{K}, \text{Na}/\text{Cl}-\text{Na}_2\text{MoO}_4$ . There was no observed linearity between the limiting current and molybdate concentration. This may be explained by the proposed formal mechanism of the electroreduction of  $\text{MoO}_4^{2-}$ -ions:



Oxygen-ions form in the acid-base reaction (I) suppress the reaction (II) or autoinhibited the electrode process. The addition of the scavengers of oxygen ions such as  $\text{Mg}^{2+}$  ( $\text{MgCl}_2$ ) to the melt  $\text{K}, \text{Na}/\text{Cl}-\text{Na}_2\text{MoO}_4$  caused an increase of wave height and changed the shape as well. The process is a diffusion controlled multielectron reduction of oxyanion  $\text{MoO}_4^{2-}$  to the metal in one stage.<sup>7</sup>

On the I-V curve of  $\text{YF}_3$  in  $\text{K}, \text{Na}/\text{Cl}$  melt showed only one wave in the potential range of  $-1.5 \pm -1.68$  V. Metallic yttrium was obtained with electrolysis at the potential of  $-1.7$  V.

On addition of all three depolarizers to the base melt ( $\text{K}, \text{Na}/\text{Cl}+\text{MnCl}_2+\text{YF}_3+\text{Na}_2\text{MoO}_4$ ) only one integrated wave could be observed in the range of  $-1.1 \pm -1.5$  V. The powder obtained with electrolysis at  $-1.5$  V, was proved to be the intermetallic compound  $\text{YMoMn}$ , in accordance with X-ray phase analysis.



**Figure 3.** Voltammograms of melts contains  $\text{YF}_3$ ,  $\text{Ca}(\text{VO}_3)_2$  and  $\text{Na}_3\text{AlF}_6$ . 1 – Base melt –  $\text{NaCl}-\text{KCl}$  (eutectic); 2 – Base melt -  $\text{NaCl}-\text{KCl} + \text{YF}_3$  ( $7 \cdot 10^{-5}$  mol  $\text{cm}^{-3}$ ); 3-Base melt -  $\text{NaCl}-\text{KCl} + \text{YF}_3$  ( $7 \cdot 10^{-5}$  mol  $\text{cm}^{-3}$ ) +  $\text{Ca}(\text{VO}_3)_2$  ( $4 \cdot 10^{-5}$  mol  $\text{cm}^{-3}$ ); 4 - Base melt -  $\text{NaCl}-\text{KCl} + \text{YF}_3$  ( $7 \cdot 10^{-5}$  mol  $\text{cm}^{-3}$ ) +  $\text{Ca}(\text{VO}_3)_2$  ( $4 \cdot 10^{-5}$  mol  $\text{cm}^{-3}$ ) +  $\text{Na}_3\text{AlF}_6$  ( $3 \cdot 10^{-5}$  mol  $\text{cm}^{-3}$ ); 5 - Base melt -  $\text{NaCl}-\text{KCl} + \text{YF}_3$  ( $7 \cdot 10^{-5}$  mol  $\text{cm}^{-3}$ ) +  $\text{Ca}(\text{VO}_3)_2$  ( $4 \cdot 10^{-5}$  mol  $\text{cm}^{-3}$ ) +  $\text{Na}_3\text{AlF}_6$  ( $3 \cdot 10^{-5}$  mol  $\text{cm}^{-3}$ ) +  $\text{MgCl}_2$  ( $3 \cdot 10^{-5}$  mol  $\text{cm}^{-3}$ ). Cathode–Pt; reference electrode–Pt. Polarization rate  $0.1 \text{ V} \cdot \text{s}^{-1}$ ,  $T=973 \text{ K}$ .

## Electrochemical synthesis of intermetallide – AlYV

To co-deposit of metallic yttrium, aluminum and vanadium, the electroreduction of  $\text{YF}_3$ ,  $\text{AlF}_3(\text{Na}_3\text{AlF}_6)$  and  $\text{CaVO}_3$  was studied in detail in  $\text{K}, \text{Na}/\text{Cl}$  melt (Fig. 3). Addition of  $\text{YF}_3$  to base melt ( $\text{K}, \text{Na}/\text{Cl}$ ) at 973 K resulted appearing a wave in the range of  $-1.5 \pm -1.68$  V. Adding of  $\text{Ca}(\text{VO}_3)_2$  to the mentioned melt resulted three waves at the  $-0.65 \pm -0.75$  V,  $-0.95 \pm -1.25$  V and  $-1.35 \pm 1.5$  V potential ranges.

The addition of cryolite to the system causing an increase in the height of the first wave and integration of the second and the third waves takes place. The wave inclined to the potential axis is obtained in the range of  $-1.1 \pm -1.7$  V. If  $\text{Mg}^{2+}$  ( $\text{MgCl}_2$ ) is added as oxygen ion scavenger to the melt, then the first wave was gradually disappeared. Finally, one wave is formed at  $-1.0 \pm 1.5$  V. The product, obtained with electrolysis performed at  $-1.5$  V is an intermetallic compound,  $\text{YAlV}$ , in accordance with X-ray phase analysis.

## Electrochemical synthesis of intermetallide $\text{YAl}_3$

On addition of  $\text{YF}_3$  ( $10^{-4}$  mole  $\text{cm}^{-3}$ ) to the  $\text{KCl}$  melt at 1073 K, only one wave is observed at voltammogram in potential range of  $-1.0 \pm -1.25$  V. Addition of  $\text{AlF}_3$  ( $10^{-4}$  mol  $\text{cm}^{-3}$ ) to the melt generates two waves were fixed at  $-0.8 \pm 1.1$  and  $-1.25 \pm -1.5$  V. When the  $\text{AlF}_3$ -concentration became equal to  $30 \cdot 10^{-5}$  mol $\cdot\text{cm}^{-3}$  only one wave could be fixed at  $-1.1 \pm -1.4$  V. An intermetallide  $\text{YAl}_3$  was obtained with electrolysis at  $-1.4$  V. This fact is confirmed by X-ray phase, micro X-ray spectral and chemical analyses.

## Electrochemical synthesis of intermetallide $\text{AlMoMn}$ .

The I-V curve of the melt  $\text{K}, \text{Na}/\text{Cl}+\text{Na}_3\text{AlF}_6$  at 973 K showed two waves in the potential ranges of  $-0.6 \pm -0.8$  and  $-1.25 \pm -1.35$  V. Addition of  $\text{Na}_2\text{MoO}_4$  to this melt resulted appearing of three waves at  $-0.7 \pm -0.8$ ,  $-1.0 \pm -1.2$  and  $-1.3 \pm -1.5$  V. Further addition of  $\text{MnCl}_2$  to the melt ( $\text{Na}_3\text{AlF}_6=1 \cdot 10^{-4}$  mol $\cdot\text{cm}^{-3}$ ,  $\text{Na}_2\text{MoO}_4=1 \cdot 10^{-4}$  mol $\cdot\text{cm}^{-3}$ , and  $\text{MnCl}_2=5 \cdot 10^{-4}$  mol $\cdot\text{cm}^{-3}$ ) gave appearance of one wave was fixed in the range of  $-1.1 \pm -1.5$  V. X-ray phase analysis of the product, obtained by electrolysis at  $-1.5$  V showed the presence of the peaks of intermetallide  $\text{AlMoMn}$ . It means, the electrochemical synthesis progressed naturally when the electroreduction of all three metals took place in a quasi-equilibrium system by mutual influence of the constituents.

## Conclusion

The intermetallides  $\text{YAl}_3$ ,  $\text{AlYV}$ ,  $\text{YMoMn}$  and polymetallic powders  $\text{CoTaMo}$  or  $\text{CoNbMo}$  were synthesized from the compounds  $\text{YF}_3$ ,  $\text{AlF}_3$ ,  $\text{MnCl}_2$ ,  $\text{Na}_2\text{MoO}_4$ ,  $\text{CaVO}_3$  or  $\text{VO}_3$  in  $\text{KCl}$ ,  $\text{K}, \text{Na}/\text{Cl}$  and  $\text{K}/\text{Cl}, \text{F}$  melts electrochemically between 873 and 1173 K. The chemical and X-ray phase analyses of obtained composites were confirmed the identity of the obtained phases.

## References

- <sup>1</sup>Li, M., Wang, J., Han, W., Yang, X., Zhang, M., Sun, Y., Zhang, M., Yan, Y., *Electrochim. Acta*, **2017**, 228, 299-307. DOI: [10.1016/j.electacta.2017.01.070](https://doi.org/10.1016/j.electacta.2017.01.070); Yan, Y., Yang, X., Huang, Y., Xue, Y., Zhang, M., Han, W., Zhang, Z., *Xiyou Jinshu Cailiao Yu Gongcheng (Rare Metal Materials and Engineering)*, **2016**, 45(2), 272-276; Zavarzin, S. V., Maslennikov, A. G., Efimov, V. A., Savinkov, Y. V., Kuz'Min, S. A., Tomilin, S. V., Osipenko, A. G., Maershin, A. A., *Radiochemistry*, **2015**, 57(6), 584-590. DOI: [10.1134/S1066362215060041](https://doi.org/10.1134/S1066362215060041); Asanov, A. M., Kushkhov, K. B., Shogenova, D. L., *Russ. Metallurgy (Metally)*, **2015**(8), 631-636. DOI: [10.1134/S0036029515080029](https://doi.org/10.1134/S0036029515080029);
- <sup>2</sup>Zhou, Z., Hua, Y., Xu, C., Li, J., Li, Y., Zhang, Q., Zhang, Y., Kuang, W., *Ionics*, **2017**, 23(1), 213-221. DOI: [10.1007/s11581-016-1810-2](https://doi.org/10.1007/s11581-016-1810-2); Liu, Y.-H., Yan, Y.-D., Zhang, M.-L., Zheng, J.-N., Yang-Zhao, Wang, P., Yin, T.-Q., Xue, Y., Jing, X.-Y., Han, W., *J. Electrochem. Soc.*, **2016**, 163(13), D672-D681. DOI: [10.1149/2.0621613jes](https://doi.org/10.1149/2.0621613jes); Hu, W., Yi, J., Zheng, B., Wang, L. *J. Solid State Chem.*, **2013**, 202, 1-5. DOI: [10.1016/j.jssc.2013.03.006](https://doi.org/10.1016/j.jssc.2013.03.006); Liu, W., Kawabe, Y., Liang, F., Okuyama, R., Lin, J., Wang, L., *Intermetallics*, **2013**, 34, 18-22. DOI: [10.1016/j.intermet.2012.11.001](https://doi.org/10.1016/j.intermet.2012.11.001);
- <sup>3</sup>Gurin, V. N., *Russ Chem. Rev.*, **1972**, 41(4), 323-340 (Russian). <https://doi.org/10.1070/RC1972v04n04ABEH002059>
- <sup>4</sup>Roginski S. Kh. *Electron events in heterogeneous catalysis*, Moscow, Nauka, **1975**, 247 (Russian).
- <sup>5</sup>Baraboshkin, A. N. *Electrocristallization of metals from molten salts* (in Russian), Moscow, Nauka, **1976**, 280.
- <sup>6</sup>Zelikman A. N., Korshunov B. G., Eljutin A. V., Zakharov A. M., *Niobium, and Tantalum*. Moscow, Metallurgia, **1990**, 296 (Russian); Konstantinov I. V., *Electrolytic preparation of tantalum, niobium and their alloys*. Moscow, Metallurgia, **1977**, 240 (Russian).
- <sup>7</sup>Gasviani N. *Foundation of electrochemical preparation of intermetallides, silicides and borides of the metals – V, Nb, Ta, Mo, Mn, Y, Al from oxyhalide melts*. Avtoreferat doktorskoi disertatsii, Tbilisi, **2006** (Georgian).

Received: 19.02.2017.

Accepted: 30.04.2017.