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MEETING POINT OF THE SCIENCE AND PRACTICE IN THE FIELDS OF
CORROSION, MATERIALS AND ENVIRONMENTAL PROTECTION

*STECIŠTE NAUKE I PRAKSE U OBLASTIMA KOROZIJE,
ZAŠTITE MATERIJALA I ŽIVOTNE SREDINE*

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PLENARY LECTURES
PLENARNA PREDAVANJA

Towards sustainable rare earth elements recovery ***Ka održivom recikliranju elemenata retkih zemalja***

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Rare-earth elements (REEs) have become extremely important to our world of technology and their sustainable supply is necessary for the transition to the clean energy economy [1,2]. As a result, the push to increase REEs availability is necessary to manage the gap between demand and supply. To supplement the REEs production slated for electronic/electrical industrial sectors and to further help the protection of the environment, recycling of Nd and other REEs will have to become a significant source of these critical metals [3–5]. Consequently, considerable efforts have been invested in different approaches toward the recovery of these critical elements from REE-containing end-of-life (EOL) products [6]. Obstacles to reprocessing the complex scrap material left behind from end-of-life resources are the absence of infrastructure, and the lack of cost-effective recycling technologies for Nd, Pr and Dy metals recovery from recycled feedstock [3,4,7]. It is understandable then that, for the time being, the strategy which is required to complete complex REE recovery processes from EOL materials must be a combination of the known methods and adaptations of the available techniques. Efforts have been made to develop a complete recycling process for NdFeB magnets, producing raw materials for remanufacturing similar magnets and closing the recycling loop. To date, the feasibility and technical aspects of REE recycling still have not been systematically evaluated [5]. However, even with considerable efforts, REE recycling processes are still not commercially viable [3].

Thus, from the viewpoint of sustainability in the coming decades, an inexpensive and environmentally friendly recycling process of REEs will certainly play an important role. Numerous papers and conference proceedings have been published focusing on the features and conditions for the possible recycling facilities of RE elements from EOL magnets [6].

So far, various approaches to the REE separation technologies have been suggested: hydrometallurgical processing [1], liquid metal extraction [8], pyrometallurgical processing [9], molten salt electrolysis (MSE) [7,10–12]. The most promising method with a strong potential to satisfy the demands is the combination of pyrometallurgical processing of the EOL materials and subsequent molten salt electrolysis of the obtained products. One of the notable advantages of electrolysis is that the process itself and especially the purity of the final products can be well controlled.

Our contribution, made in joint research efforts of ICTM Institute, University of Belgrade with IME Institute, Aachen University, to the molten salt electrolysis within the field of recycling rare earth metals from end-of-life NdFeB magnets containing significant amounts of rare earth elements, was focused on the Nd-Pr alloy formation that could be fed directly back to the vacuum alloying step in the production of the new NdFeB magnets. In order to make extracting of individual rare earth metals for reuse in magnets or other materials economically viable, additional knowledge onto the electrodeposition of Nd and Pr from molten fluoride electrolyte had to be acquired. We started the investigation with the reaction mechanism of Nd electrodeposition, Fig. 1. [12,13], and continued with simultaneous electrodeposition processes of neodymium and praseodymium [10,11,14].

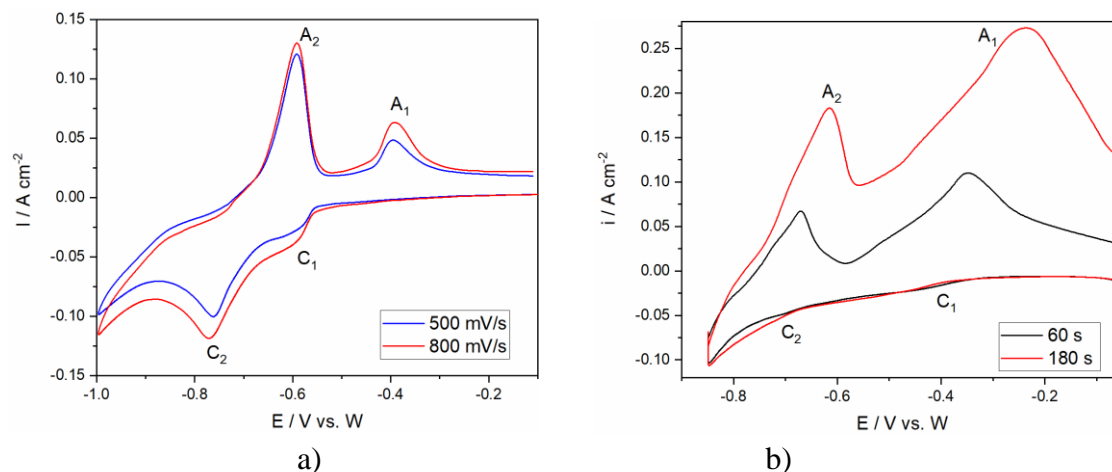


Figure 1. Cyclic voltammograms recorded on Mo cathode in 87.5 wt.% NdF_3 + 12.5 wt.% LiF + 2 wt.% Nd_2O_3 molten salt electrolyte, at 1323 K: (a) potential range from -0.100 V to -1.000 V vs. W scanned with different sweep rates; (b) Voltammograms obtained with different “holding times” ($t = 60$ and 180 s) at the cathodic end potential of the cycle $E_F = -0.850 \text{ V}$ vs. W, sweep rate = 100 mVs^{-1} .

Our study was focused on the fundamentals underlying the electrochemical reduction of both Nd(III)/Nd(0) and Pr(III)/Pr(0) in the oxide-fluoride melt using tungsten (W) or molybdenum (Mo) working electrode, glassy carbon counter electrode (GC anode) and W reference electrode. The electrochemical reduction process of Nd(III) ions in the systems investigated has been identified as a two-step process via Nd(II). Actually, neodymium Nd(III) ions were electrochemically reduced in two consecutive steps: $\text{Nd(III)} + e^- \rightarrow \text{Nd(II)}$ (reflected by the cathodic current wave C_1 on CV, Fig. 1. a) and b)) and $\text{Nd(II)} + 2e^- \rightarrow \text{Nd(0)}$, (ascribed to the cathodic current wave C_2 on the CV from Fig. 1. a) and b)). As soon as the first amounts of Nd metal were electrodeposited on the working electrode, the following disproportionation (comproportionation) reaction takes place with the electrolyte and leads to [10–13]:



Under the same conditions, praseodymium electrodeposition is a single step process $\text{Pr(III)} + 3e^- \rightarrow \text{Pr(0)}$ (ascribed to the cathodic current wave C_3 on the CV, Fig.2.) following the neodymium deposition [10,11]. Detailed studies of the Nd and Pr cations redox transitions to their metal forms during electrodeposition from fluoride based molten salt enriched with REO revealed that electrochemical steps are under mixed control: by ion mass transfer and charge transfer rate involving the decomposition of their ligand shells.

After initial results, our aim was to achieve better deposition efficiency by increasing the quantity of neodymium and praseodymium metal remaining on the working electrode surface after the deposition, to improve control of the electrodeposition process and to reduce the greenhouse gas emission during electrolysis. To make this possible, a ternary phase diagram was constructed for the liquidus temperatures of the chosen fluoride based molten salts, $\text{NdF}_3 + \text{PrF}_3 + \text{LiF}$ [11]. This step was necessary to obtain an improved prediction of the optimal electrolyte constitution, and to avoid issues related to inappropriate composition and high melting temperatures of the mixture required for the process realization.

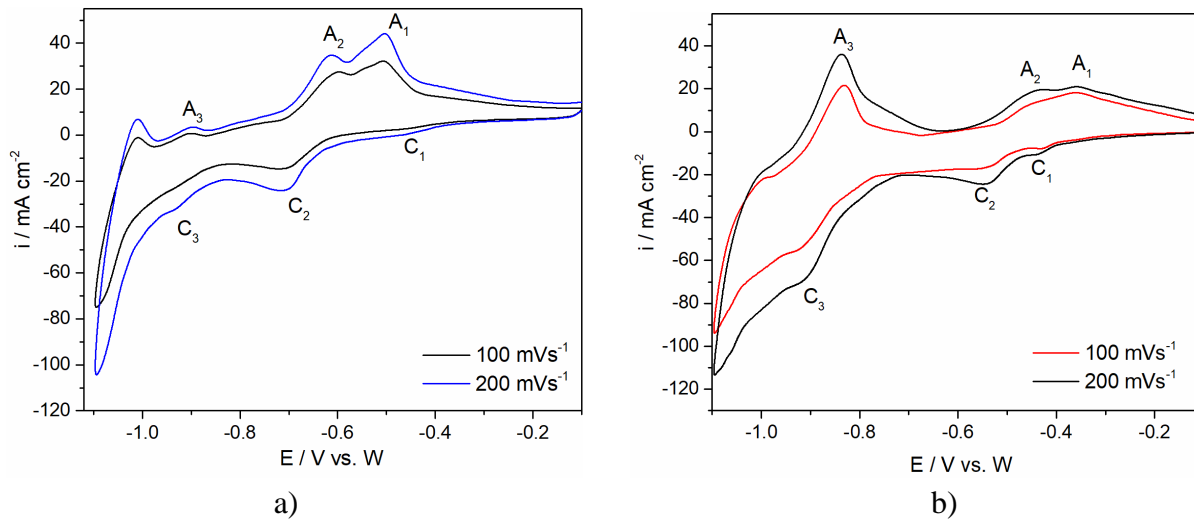


Figure 2. Cyclic voltammograms recorded on W working substrate starting from initial potential $E_I = -0.100$ V to final cathodic end potential $E_F = -1.100$ V vs. W. Voltammograms were obtained with different sweep rates at 1323 K in 45.5 wt.% NdF_3 + 45.5 wt.% PrF_3 + 9 wt.% LiF electrolyte containing different RE oxide concentrations added: (a) 1 wt.% Nd_2O_3 + 1 wt.% Pr_6O_{11} ; (b) 2 wt.% Nd_2O_3 + 2 wt.% Pr_6O_{11} .

To address the suitability of the chosen electrolyte, system chemical composition and optimal process conditions, the concentration of the REO added to the fluoride based NdF_3 + PrF_3 + LiF electrolyte was varied in order to precisely determine the adjustable parameters, Table 1.

Obtained results were encouraging. The electrodeposition mechanism for each RE (Nd and Pr) was identified, and the deposition efficiency of each element was improved, Figures 3. and 4.

Table 1. Electrolyte composition

Electrolyte	Components	Weigh percentage (wt.%)	REO content (wt%)		Literature
			Nd_2O_3	Pr_6O_{11}	
			E-1	NdF_3 LiF	
E-2	NdF_3	63.17	1	1	[10]
	LiF	12.02	2	2	
	PrF_3	20.96			
E-3	NdF_3	45.5	0.5	0.5	[11]
	LiF	9.0	1	1	
	PrF_3	45.5	2	2	

EPMA mapping of the sample's cross-section after Nd and Pr co-deposition revealed that most of neodymium and praseodymium metals were distributed in the area next to the working electrode substrate, Figs. 3.a) and b).

This area represents a thin layer of Nd and Pr metals, approximately 40 mas % neodymium and 40 mass % Pr, deposited on the electrode surface. In these areas, oxygen and fluoride were present in the lowest recorded concentrations, Fig. 3.c).

Continuing the series of fundamental studies on Nd and Pr co-deposition from the fluoride melts, allowed us to build experimental and theoretical knowledge, which would allow to forecast the viability of extracting rare earth metals from end-of-life NdFeB magnets.

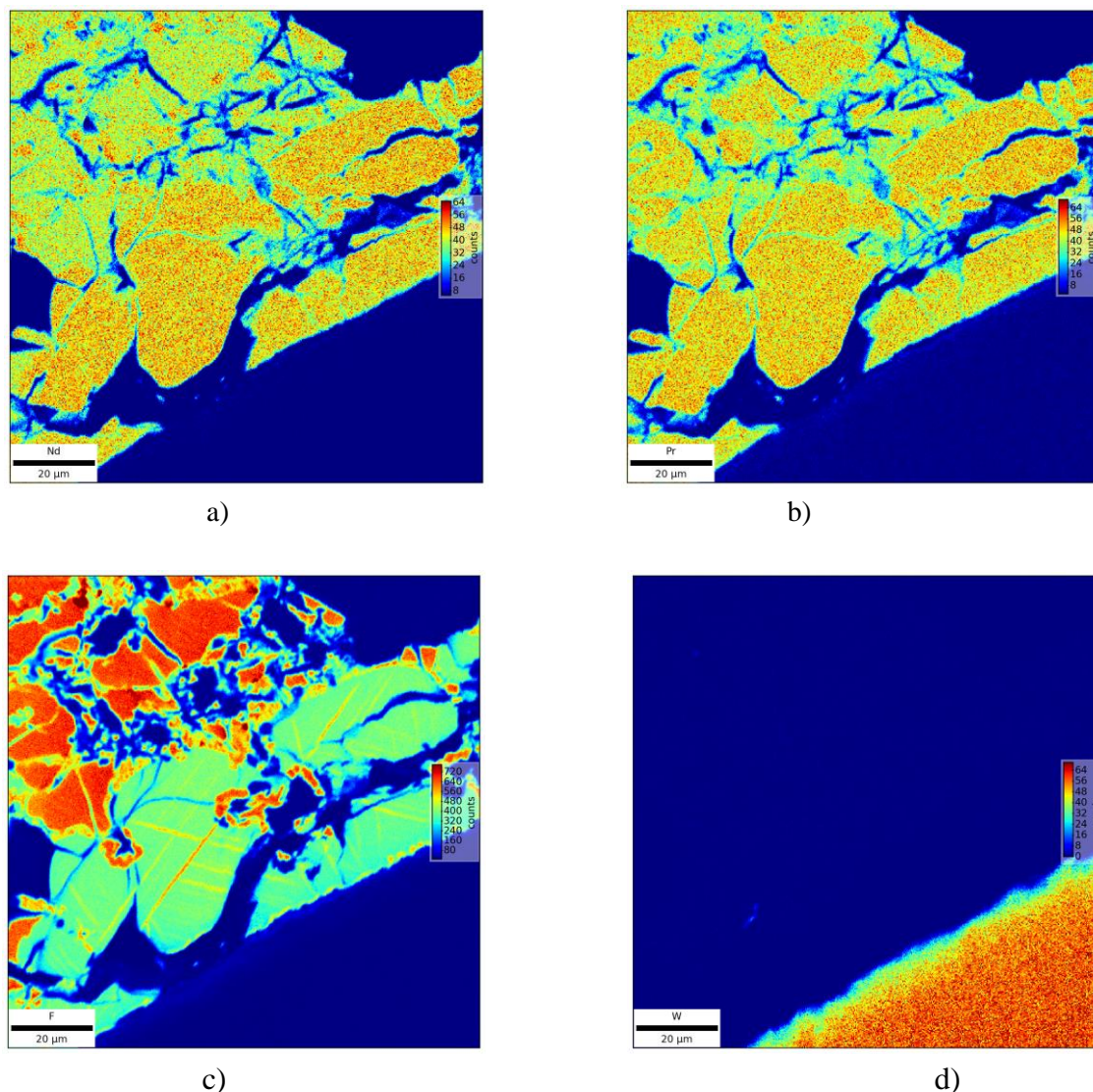


Figure 3. EPMA mapping of the sample after deposition at -0.900 V vs. W on a W cathode from molten 45.5 wt.% NdF_3 + 45.5 wt.% PrF_3 + 9 wt.% LiF + 0.5 wt.% Nd_2O_3 + 0.5 wt.% Pr_6O_{11} electrolyte for 240 min. at 1323 K, showing distribution: (a) Pr; (b) Nd; (c) F; (d) W.

Additionally, scanning electron microscopy (SEM) revealed insight into the deposited material and energy dispersive spectroscopy (EDS) confirmed the presence of Nd and Pr metals on the working electrode substrate. The weight % of all elements in the deposit detected by EDS analysis are summarized in Table 2.

Table 2. Elemental analysis (in weight %) of the electrodeposits obtained.

Elements in weight %						
	O	F	Pr	Nd	W	Total
Spectrum 1	4.77	25.51	28.78	29.72	11.21	100
Spectrum 2	5.48	24.78	34.30	35.45	-	100

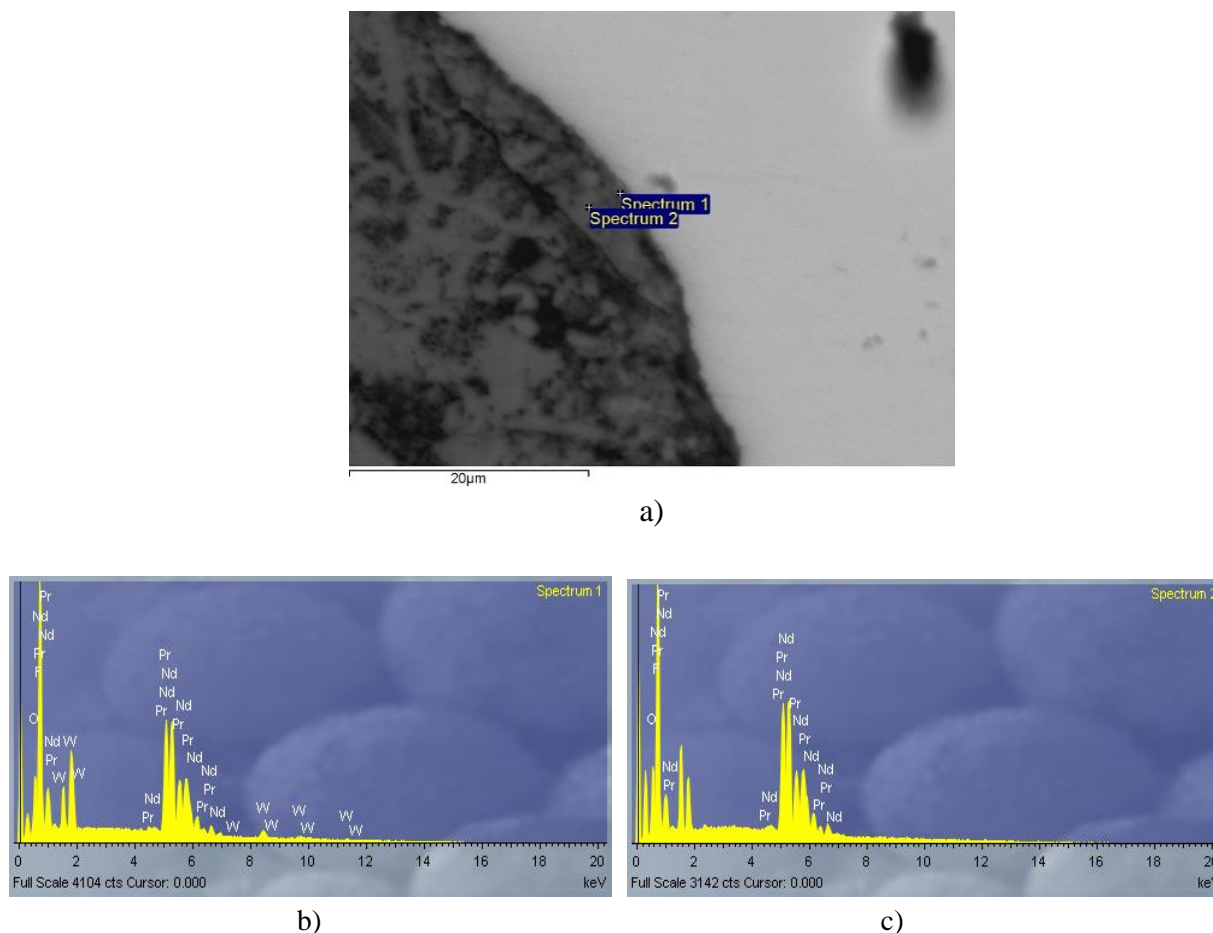


Figure 4. a) SEM micrographs of deposits obtained by electrodeposition at -0.900 V vs. W on a W cathode from molten 45.5 wt.% NdF_3 + 45.5 wt.% PrF_3 + 9 wt.% LiF + 0.5 wt.% Nd_2O_3 + 0.5 wt.% Pr_6O_{11} electrolyte, for 240 min. at 1323 K; b) and c) EDS spectra of the deposit obtained.

Two general steps in this process of recycling rare earth metals are, the production of magnet recycling-derived oxide (MRDO) followed by molten salt electrolysis. It is important to note that these two steps are integrated. The proposed process uses the advantage of the obtained REE alloy metallic phase which consists of the REE and iron ready to be further used directly in the NdFeB magnet production.

We prepared MRDO from the spent NdFeB-magnets in two steps [9,15]. First step was oxidation of the spent NdFeB magnets into mixed rare earth, iron, boron... oxide containing form [15]. In the second step, by using the reductive smelting process, a substantial amount of iron present in the metal phase was removed from the oxidized magnets [9]. At the end of reductive smelting step, the ICE-OES and XRD analysis were conducted on both phases. According to those analyses, the metal phase showed a maximum Fe content of 92.3 wt.%, while the slag phase (MRDO) showed a maximum total REE (Nd, Pr, and Dy) content of 47.47 wt.%, both obtained at a smelting temperature of 1773 K [9].

To complete the process of recycling the NdFeB magnet, MRDO was used as a source of the rare earth oxides in fluoride-based baths during the molten salt electrolysis process [16]. Under the applied conditions, Nd and Pr were electrodeposited in metal form from the electrolyte composed of rare earth oxides present in the MRDO dissolved in the corresponding rare earth fluoride salts [16].

Although there are many parameters that should be addressed for a direct implementation of this method on an industrial scale, with this particular approach we confirmed the viability of using

MRDO in the electrolysis as a part of fluoride molten salt electrolyte and finally established the route for recycling rare earth elements from used magnet scrap.

Finally, in an effort to develop a more efficient electrochemical deposition process, we chose low-deposition overpotential to suppress greenhouse gas emissions and to achieve high-purity Nd and Pr metal production on the working substrate [10–13].

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