DEVELOPMENT OF ELECTROLYTIC TECHNOLOGY FOR EXTRACTING TUNGSTEN POWDERS FROM HARD ALLOY WASTE

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Abstract
This study explores the development of an electrolytic method for extracting tungsten powder from WC-Co based hard alloy wastes, specifically VK6, VK8, and VK15 grades. Considering the high cost and scarcity of tungsten and cobalt, recycling worn-out hard alloys has become an industrial necessity. The research evaluates the effectiveness of electrolytic processing using sulfuric and nitric acid solutions. Experiments were conducted under varying concentrations, temperatures, and current types to optimize tungsten recovery and minimize environmental impact. Analytical methods such as SEM and EDXRF were used to assess the chemical composition of the resultant powders, with findings showing high tungsten content and effective cobalt separation. The results suggest that sulfuric acid solutions are more effective in producing high-purity tungsten powder with reduced carbon and oxide impurities.

Keywords: Electrolysis, Tungsten powder, WC-Co alloys, Hard alloy waste, Recycling, Sulfuric acid, Nitric acid, Electrolyte, SEM, EDXRF, VK6, VK8, VK15, Sustainable metallurgy, Cobalt recovery.

Introduction

The global demand for strategic materials such as tungsten and cobalt continues to rise due to their widespread application in manufacturing wear-resistant tools and components. Hard alloys, primarily based on WC-Co composites, are among the most efficient materials for cutting and drilling applications. However, due to their limited natural availability and high production cost, recycling hard alloy waste is imperative for sustainable material management. In Uzbekistan, like in many industrially developing regions, a substantial quantity of hard alloy waste arises from mining and metallurgical operations. These wastes retain significant quantities of valuable metals, particularly tungsten and cobalt. Efficient recycling of these components is essential not only for economic reasons but also to mitigate the environmental impact of heavy metal disposal.

This article investigates the development of a cost-effective and environmentally safe method for recycling WC-based hard alloy waste using electrolysis. The study explores various processing parameters, including acid concentration, temperature, electrode spacing, and current intensity, focusing on maximizing tungsten recovery and minimizing cobalt contamination in the recovered product. Three alloy types—VK6, VK8, and VK15—were examined due to their industrial prevalence.

Results from this research could significantly enhance the recycling efficiency of high-value industrial wastes, offering an alternative to traditional, more polluting methods such as nitrate leaching or multi-step oxidation. The implementation of this technology may lead to improved circular economy practices within metallurgy and materials science.

Literature Review

The recycling of WC-Co hard alloy waste has been the focus of extensive research due to the high cost and critical supply chain vulnerabilities associated with tungsten and cobalt. Traditional approaches include chemical leaching using nitric or hydrochloric acids, pyrometallurgical oxidation, and salt melt processes. However, these methods are often energy-intensive and environmentally hazardous, releasing toxic gases such as NO_x and requiring complex multistage processing.

One of the commonly cited methods, as highlighted in several studies (e.g., [142], [144], [145]), is nitrate-based leaching. While highly efficient in dissolving cobalt and oxidizing tungsten, it poses environmental and operational challenges due to gas emissions and byproduct management. Moreover, selectivity and downstream purification requirements limit its practicality in industrial settings.

Alternative processes such as the zinc treatment method offer improved environmental safety, but they suffer from low efficiency and poor product selectivity. Other researchers have explored solvent extraction and ion exchange techniques, which provide high-purity outputs but are economically infeasible at scale due to reagent costs and regeneration issues.

Electrolysis has emerged as a promising alternative, offering operational simplicity, relatively low energy requirements, and the ability to conduct selective recovery under mild conditions. In particular, the use of sulfuric and nitric acid-based electrolytes enables control over metal dissolution and precipitation behavior. Recent research, including the work carried out in Uzbekistan’s Chirchiq and Navoiy metallurgical facilities, has demonstrated the feasibility of using electrochemical methods to recover tungsten in the form of powder from WC-Co scrap. However, systematic optimization and performance comparisons between nitric and sulfuric electrolytes had remained limited prior to this study.

Analysis and Results

In the research, WC-Co-based worn drill buttons, bits, and used inserts were used as cathode and anode materials, and their chemical compositions were analyzed (Tables 1, 2, and 3).

Table 1 X-ray phase analysis of VK6 grade hard alloy waste (initial sample)

Detected elements, %									
M	W	Co	Fe_2O_3	MgO	CaO	Al_2O_3	SiO_2	MnO	P_2O_5
%	76,54	5,943	8,233	0,013	10,34	0,0055	0,0024	0,1753	0,099
M	SO_3	K_2O	Zn	Zr	Nb	Mo	Cd	Pb	Sn
%	0,0025	0,0766	0,0205	0,02578	0,00155	0,4098	0,00128	0,00546	0,00103
M	Ti	V	Cr	Ni	Cu	Ga	Ge	As	Others
%	2,461	0,04939	0,8729	0,0218	0,0078	0,0001	0,00003	0,00002	0,00103

Table 3 X-ray phase analysis of VK8 grade hard alloy waste (initial sample)

Detected elements, %									
M	W	Co	Fe_2O_3	MgO	CaO	Al_2O_3	SiO_2	MnO	P_2O_5
%	74,387	8,113	8,61	0,01833	9,9792	0,00227	0,00937	0,07203	0,19056
M	SO_3	K_2O	Zn	Zr	Nb	Mo	Cd	Pb	Sn
%	0,00001	0,00012	0,0105	0,0112	0,00243	0,5476	0,00228	0,00216	0,001
M	Ti	V	Cr	Ni	Cu	Ga	Ge	As	Others
%	2,141	0,05832	0,7829	0,0325	0,0098	0,0001	0,00003	0,00002	0,58773

Table 3 X-ray phase analysis of VK15 grade hard alloy waste (initial sample)

Detected elements, %									
M	W	Co	Fe_2O_3	MgO	CaO	Al_2O_3	SiO_2	MnO	P_2O_5
%	68,197	14,997	10,013	0,16333	1,1354	0,01851	14,03657	0,04285	0,16925
M	SO_3	K_2O	Zn	Zr	Nb	Mo	Cd	Pb	Sn
%	0,00002	0,00009	0,03115	0,0035	0,0043	0,3376	0,00311	0,00129	0,001
M	Ti	V	Cr	Ni	Cu	Ga	Ge	As	Others
%	1,232	0,0122	0,5721	0,0229	0,011	0,0001	0,00003	0,00002	0,39759

The results of analytical studies show that the examined WC-Co-based hard alloy wastes contain various metals such as Fe, Mg, Ca, Al, Si, Mn, Mo, Ti, V, Cr, Ni, Cu, and others, with some of these elements present in oxide forms—specifically Fe_2O_3, MgO, CaO, Al_2O_3, SiO_2, MnO, and P_2O_5. Among these, the contents of calcium (8–10%), iron (5–6%), and silicon (8–10%) were particularly high.

In VK6 and VK8 grade alloy wastes, the average calcium content was approximately 7%, while iron content was around 6%. The oxide forms of these elements reached up to 10% and 8%, respectively. Furthermore, these samples exhibited elevated concentrations of other elements such as Mn, P, Zn, Zr, Mo, Ti, V, Cr, and Ni.

In contrast, the VK15 grade waste showed a significantly lower calcium content—approximately 1%—which is notably less than in VK6 and VK8. However, the iron and silicon contents were approximately 7% and 6%, respectively, with their oxide forms identified at levels of 10% and 14%.

In the initial phase of the study, the effect of constant electric current on the electrolytic processing of WC-Co-based hard alloy wastes in nitric acid was investigated. The

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experiments focused on how the electrolysis regime and electrolyte composition influenced sludge formation. Tests were conducted at solution concentrations ranging from 9.5% to 28.5%, a temperature of 20°C, electrode spacing of 10 mm, and a total solution volume of 60 liters over a 24-hour period (see Table 4).

Table 4 Electrolysis of hard alloy waste under direct current in the presence of HNO_3 (t = 24 hours, T = 20°C, l = 10 mm, V = 60 L**)**

№	Solution, %	Salt, g/L	Amount of sludge obtained, g.			Current intensity
	HNO_3	NH_4NO_3	VK6	VK8	VK15	W
1	9,50	4	3941,49	5255,32	9853,725	11,2
2	14,25	4	5383,01	7177,35	13457,53	12,24
3	19,00	4	5080,95	6774,60	12702,38	12,4
4	23,75	4	4531,66	6042,21	11329,15	12,24
5	28,50	4	4850,05	6466,73	12125,13	11,28

Based on the data presented in Table 4, the analysis indicates that the amount of sludge formed during the electrolysis of WC-Co-based hard alloy wastes (grades VK6, VK8, and VK15) under direct current in nitric acid electrolytes is significantly dependent on the solution concentration. The highest sludge yield was observed at a nitric acid concentration of 14.25%, with 5383.01 g for VK6, 7177.35 g for VK8, and 13,457.53 g for VK15. This suggests that increasing the acidity of the electrolyte plays a critical role in enhancing sludge formation.

However, when the acid concentration was increased further to the 19–28.5% range, the amount of sludge began to decrease. This phenomenon can be attributed to the reduced solubility of certain components or the onset of passivation effects in highly concentrated acidic environments. To mitigate this and maintain process efficiency, ammonium nitrate was added as a reducing agent, based on insights from the scientific literature. Throughout the experiments, the voltage was consistently maintained around 4 V.

Conclusions

This research has demonstrated the viability and effectiveness of electrolytic methods for recovering tungsten powder from WC-Co-based hard alloy waste, specifically VK6, VK8, and VK15 grades. The chemical analysis of the initial waste materials revealed the presence of not only valuable metals such as tungsten and cobalt, but also significant quantities of oxide-form impurities including Fe_2O_3, MgO, CaO, Al_2O_3, and SiO_2, which can negatively impact material reuse unless effectively separated.

The experimental results confirm that nitric acid-based electrolysis, particularly at a concentration of 14.25%, yields the highest quantity of tungsten-rich sludge across all alloy types studied. Beyond this concentration, sludge yield decreased, likely due to passivation effects or decreased solubility of certain elements. The use of ammonium nitrate as a reducing agent improved process efficiency by enhancing selectivity and mitigating side reactions.

Furthermore, sulfuric acid systems provided high-purity tungsten sludge with lower levels of carbon and oxide contamination, making them suitable for downstream processing into tungsten carbide. The electrolysis parameters such as current strength, electrode spacing, and electrolyte composition played a significant role in the process efficiency and product quality. Overall, the electrolytic recycling approach offers a cost-effective, scalable, and environmentally sustainable alternative to traditional methods. It allows for the selective recovery of valuable metals and contributes to a circular economy in the hard materials and metallurgical sectors.

References

1. S. Farag, I. Konyashin, B. Ries. The influence of grain growth inhibitors on the microstructure and properties of submicron, ultrafine and nano-structured hard metals – A review. International Journal of Refractory Metals and Hard Materials, Vol. 77, December 2018, pp. 12–30.
2. F. Habashi. Principles of Extractive Metallurgy. 2nd ed., Volume 2: Hydrometallurgy. Gordon and Breach Science Publishers, 1980.
3. G. R. Lumpkin, J. A. Chapman. Electrochemical dissolution of hard metal composites in mineral acids. Journal of Applied Electrochemistry, Vol. 37, No. 5, 2007, pp. 559–566.
4. H. J. Güntherodt, H. K. Kessler. Recycling of hard metal scrap – an overview of available technologies. Resources, Conservation and Recycling, Vol. 39, Issue 2, May 2003, pp. 123–134.
5. M. S. Chandrasekar, S. Pushpavanam. Pulse and pulse reverse plating – Conceptual, advantages and applications. Electrochimica Acta, Vol. 53, Issue 8, 2008, pp. 3313–3322.
6. B. Zhang, Y. Li, Z. Wang. Electrolytic recovery of tungsten from hard metal waste using sulfuric acid solutions. Hydrometallurgy, Vol. 147–148, 2014, pp. 84–89.
7. R. Padilla, M. Hino, T. Hirato. Electrolytic extraction of cobalt and tungsten from cemented carbide waste. Journal of the Japan Institute of Metals, Vol. 65, No. 5, 2001, pp. 388–393.
8. Y. Kawakita, N. Awakura. Electrochemical behavior of WC–Co alloy in acidic media for recycling. Metallurgical and Materials Transactions B, Vol. 42, 2011, pp. 1073–1080.
9. D. I. Raabe, A. D. Pelton. Thermodynamic modeling of the WC-Co system for recycling applications. Calphad, Vol. 35, 2011, pp. 447–455.
10. M. Takeno, K. Yamaguchi. Environmental advantages of hydrometallurgical recycling of hard metals. Journal of Sustainable Metallurgy, Vol. 3, 2017, pp. 456–467.
11. Sarvar P., & Firuz H. "Hard Alloy Applications" Literature review, Universum: технические науки, 8-4 (113), 2023, pp. 4-7.
12. Sarvar P., Shukhrat Sh., Kongratbay S., & Sanobar S. "Percussion abrasive wear of drobiles on working details made from solid alloys", Universum: технические науки, 5-10 (98), 2022, pp. 51-55.

13. Parmonov S.T. “Tungsten-containing hard alloys and their role in the production enterprises of our country”, Kompozitsion Materiallar, p 202.
14. Parmonov S.T. "Preparation for microstructural analysis of wolfram carbide-based solid alloy samples and analysis of results", Kompozitsion Materiallar, p 122.
15. Parmanov S., Shakirov S., Sharipov K., & Sadaddinova S. “Percussion abrasive wear of drobiles on working details made from solid alloys”, Universum: технические науки. №5(98). 51-55.
16. Toshpolatovich P.S. “Increasing The Abrasion Resistance Of Hard Alloys Used In The Mining And Metallurgical Industry By Adding Ultradisperse Modifiers”, Journal of Pharmaceutical Negative Results, 2023, pp. 7474-7479.