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**ENERGY-SAVING AND ENVIRONMENTALLY-FRIENDLY
METHODS EXTRACTION OF TUNGSTEN AND TUNGSTEN ORE
CONCENTRATE - AN INTEGRAL PART OF ENVIRONMENT AND
HUMAN HEALT**

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Tungsten carbide–cobalt hard alloys were first cermets that found an industrial application. The high importance of these materials has not become lower until now. To return the valuable components of hard alloys to the production industry, it is necessary to find a way of recycling the waste materials containing these components. These waste materials can be represented by matrices of drilling and cutting tools and by scrap. Because of the high cost and, sometimes, deficit of tungsten and cobalt, the problems of developing new methods of recycling lumps of waste hard alloys have become of high concern recently [1–3]. The existing methods of extracting the components of hard alloys differ from each other by not only the treatment mode but also the nature of the applied chemical reactants [4]. The essential disadvantage of the methods of dissolving the components of hard alloys with various acids and their mixtures is the toxicity of the applied reactants. This disadvantage is partially eliminated by treating waste diamond and hard alloy tools with anodic dissolution in hydroxide–chloride melts [5]. In this case, the tungsten and carbon transfer into the melt in the form of tungstate, niobate and carbonate, respectively, and the impregnating materials for the hard-alloy matrix accumulate at the cathode in the form of finely dispersed metal powders. The end product of the proposed method is tungsten oxide of metals, which requires further treatment to be returned into the process of manufacturing hard-alloy tools.

The results of using the method of high-temperature selective extraction of tungsten from the concentrates and waste materials in halide–silicate melts are reported by [6].

Tungsten compounds are usually extracted from ores and concentrates by dissolution in different acids, the environmental danger and technological ineffectiveness of which are obvious. High-temperature selective extraction in nonaggressive salt melts can be suggested as an alternative method. The method of

producing tungsten carbide by treating tungsten-containing melts by reducing gases, carbon or calcium carbide has recently been developed. Its first step is usually the decomposition of the ore or concentrates by the method of high-temperature selective extraction. Sodium chloride and sodium silicate melts can be recommended as extracting components. When they are melted together with, for example, tungsten (wolframite or scheelite) concentrates, the tungsten compounds are transferred into the chloride phase while the oxides of iron, manganese, and calcium are transferred into the silicate phase. The phases are separated by selective decantation. The degree of extraction of refractory metals into the chloride phase largely determines the further profitability of the method of producing refractory metals carbide by treating the melts with gases.

In the present paper, we will study the method of high-temperature selective extraction of tungsten from its concentrates and determine the most effective conditions (temperature, melt composition, extraction duration) for operating the process.

Optimal compositions of the alloy that provide the maximum efficiency of extracting tungsten from the halide-tungstate phase and its separation from iron and manganese oxides were found experimentally. The concentrations of NaCl, Na₂SiO₃, and, for example, (Fe, Mn)WO₄ for the separation of two immiscible liquids were chosen according to the recommendations given in paper [7-11]. Figures 1a and 1b illustrate the influence of the concentrations of sodium chloride in the range of 35 to 60 wt % and sodium metasilicate in the range of 10 to 40 wt%. An extraction efficiency as high as 99% and the highest separation ratios were obtained for the melt containing (wt%) 45 NaCl, 20 Na₂SiO₃, and 35 (Fe, Mn)WO₄. The chemical composition of the phases and the distribution of the major components between them after high-temperature selective extraction are listed in Table 1. Taking into account the molar ratio of components in the charge, the reaction for high-temperature selective extraction can be written, for example, as:

$$(\text{Fe, Mn})\text{WO}_4 + \text{Na}_2\text{SiO}_3 \rightarrow \text{Na}_2\text{WO}_4 + (\text{Fe, Mn})\text{SiO}_3.$$

The high technological effectiveness of high-temperature selective extraction may be attributed to the capability of sodium tungstate to mix with sodium chloride in any proportions [12,13] and the immiscibility of the silicate phase having a melting point lower than 1000°C with the halide-tungstate phase [14].

The most effective method of processing scheelite concentrates is the high-temperature selective extraction of its mixture with wolframite in the proportion from 1 : 4 to 2 : 1. The use of these mixtures makes it possible to effect the process of high-temperature selective extraction without introduction of fluxes (usually used in the form of alkaline-earth metals and aluminum oxide, which is necessary for the processing of scheelite) [15]. The use of the mixture composed in the indicated proportions makes it possible to extract more than 96% of WO₃ into the

halide-tungstate phase. The content of calcium, iron, and manganese oxides in the latter was less than 2.5 wt%. The halide-tungstate phase for the combined concentrates contained (wt%) 29–32 WO_3 , 0.03–0.12 CaO , 0.02–0.05 Fe_2O_3 , and 0.01–0.04 MnO_2 .

Conclusions

It is shown that tungsten is extracted from tungsten ores and concentrates in sodium chloride–sodium metasilicate melts into the halide phase at a temperature of 1050 to 1050–1100°C. The compositions of the melts that provide the extraction efficiency as high as 99% and maximal ratios of separation of the components between the phases are chosen.

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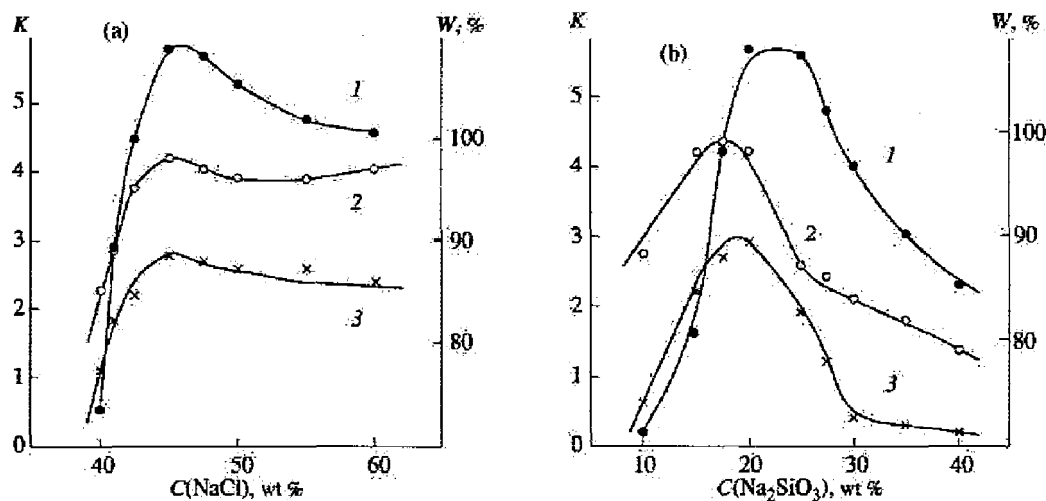


Fig. 1. Effect of the concentrations of (a) NaCl and (b) Na_2SiO_3 on (1, 2) separation ratio k and (3) efficiency W of WO_3 extraction into the halide phase

Table 1. Chemical compositions of phases and the distribution of major components between them

Phase	Component, wt%		
	WO ₃	FeO	MnO
Chemical composition:			
Halide	31,20	0,21	0,33
Silicate	0,35	10,31	27,70
Distribution:			
Halide	99,61	7,32	3,65
Silicate	0,39	92,68	96,35