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Some Processing Techniques for Rhenium Isolation and Purification from Refractory Alloys

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Abstract

Two variants are presented for the hydrometallurgical extraction of rhenium from the solutions of complicated composition, obtained *via* recycling the wastes of multicomponent refractory alloy ZhS-32. The applying of both schemes results in the formation of AR-0 grade NH_4ReO_4. The yield of the metal amounts to 99.2 % from the initial metal content in the alloy. The techniques used allow performing a single stage separation of the rhenium from impurity metals with eliminating the channels of the irretrievable loss thereof.

Key words: refractory alloy, hydrometallurgy, nonferrous metals, rhenium, segregation, separation, purification

INTRODUCTION

The most large-scale field of using the entire world's production of rhenium consists in the production of binary platinum-rhenium catalysts for reforming the oil fractions and producing high-temperature alloys. These special alloys are used find their application in the manufacture of gas turbine blades and other types of high-temperature composites for nuclear, missile and aircraft engineering. Recycling them would help to remove the gap between supply and demand all over the world with respect to this element that is not only the rarest, but also extremely dispersed one. The modern original methods under development intended for the isolation of rhenium from waste materials suggest increasing the purity and range of the compounds thereof in comparison with the production from primary raw materials. These compounds could be successfully used, for example, in rhenium powder metallurgy for improving the operational performance of different products.

EXPERIMENTAL

The ability of rhenium to be dissolved rapidly and quantitatively in oxidizing environments containing H_2O_2 or HNO_3 is well-known [1]. Such a purely chemical etching of the mentioned alloys is extremely slow even when using aggressive aqua regia. Initial solutions for the isolation of rhenium were obtained in nitric oxide media with the initial concentrations of HNO_3 ranging within 3.9–4.7 mol/L under alternating electric current ($I = 9$ A, $U = 60$ V). Such methods for transferring Re, Mo and W into the soluble state via anodic oxidation under the action of the direct current in alkaline electrolytes are known from the literature [2, 3]. The authors point out some disadvantages of the method associated with a low productivity of the dissolution process due to a low electrical conductivity of ammonia environments.

In our case, the source solutions for the isolation and purification of rhenium represented the filtrates from leaching the blades of turbines made of alloy ZhS-32. The ZhS-32 alloy has the following composition (mass %): Re 4.0, Ta 4.0, Al 10.0, Co 6.5, W 10.0, Cr 5.0, Mo 1.5, Nb 2.0, Ni 40.0. The processing resulted in passing approximately 2/3 of the mass of the sample into the liquid phase that contains great amounts of Ni(II), Co(III), Cr(III) and Al(III) nitrates of against the background of the residual content of free HNO_3 (about 0.1 mol/L). The chemical analysis of the sludge formed indicates that it involves almost the entire initial amount of W, Nb, Mo and Ta. Depending on the conditions of the experiment the average content of Re in the working solutions obtained, as determined by atomic absorption, is not less than 7.0 g/L.

RESULTS AND DISCUSSION

The literature describes a variety of methods for the technological isolation of rhenium and its deep purification: ion exchange, extraction, precipitation, cementation, absorption, electrolytic and electro-membrane methods, *etc.* The main feature of the methods listed consists in a prevailing focus on purifying the rhenium from concomitant molybdenum. In our case, the range of impurity elements is wider to a considerable extent, which requires for using any convenient methods for the group separation of the prevailing metal impurities. As it follows from the scheme of sulphide-based rhenium extraction process (Fig. 1), after obtaining the filtrate a standard reaction of rhenium sulphidation by solid crystalline hydrate Na_2S is performed with the formation of insoluble Re_2S_7, which reaction occurs with a maximum yield in acidic solutions. All the other metals belonging to the third analytical group exhibit the formation of sulphides soluble in HCl [4].

It is just the chemical treatment that allows one to implement in practice the difference between the chemical behaviour of rhenium heptasulphide and the sulphides of other metals. The further stages of dissolving the Re_2S_7 precipitate formed and thoroughly washed with water to produce $HReO_4$ with the isolation of necessary salts and purification procedures are meant to be trivial. Such a procedure of rhenium concentration and separation at the beginning of the process *via* the formation of water-insoluble rhenium heptasulphide use to be performed in many commercially developed industrial technological processes using a wide variety of sulphidation reagents: H_2S, Na_2S, $(NH_4)_2S$, $Na_2S_2O_3$ or $CH_3C(S)NH_2$. At the same time, it should be noted that there is an increase in the completeness of rhenium isolation in the form of Re_2S_7 in the course of performing this process in the environment of reducing agents such as $N_2H_4 \cdot 2HCl$ or $NH_2OH \cdot HCl$ [5], however no explanation for this phenomenon was presented. A contemporary scientific vindication of this fact is based on a more detailed investigation of the charge state of rhenium and sulphur those compose the structure of Re_2S_7. The authors of [6] using the results of EXAFS experiments (Extended X-ray Absorption Fine Structure) evidenced that Re2S7 has a polymeric structure involving Re(VII) ions, disulphide sulphur (S–S) and Re(V).

Thus, the main conclusion resulting from their studies consists the fact that the quantitative extraction of Re in the form of Re_2S_7 requires the reaction solution to contain a reducing agent capable of reducing the oxidation state of some rhenium atoms down to 5+. The most suitable reducing agent for operating in such reaction media, according to the authors of [7] is presented by hydroxylamine sulphate. Therefore, the basic principle of rhenium separation in the first variant of the method consists in a selective transforming it into the solid phase at the beginning of the process. The main metal impurities in this case remain in the solution.

The second variant involves first of all obtaining a collective precipitate of Ni(II), Cr(III), Co(III), Al(III) hydroxides and holding the rhenium in solved state. In order to perform this, the initial polymetallic solution is neutralized with dry $NaHCO_3$ under heating to attain the value of pH ~ 9. The resulting precipitate is filtered off after coagulation with further thoroughly washing by distilled water from $[ReO_4]^-$ ions in the solution those are capable of ad-

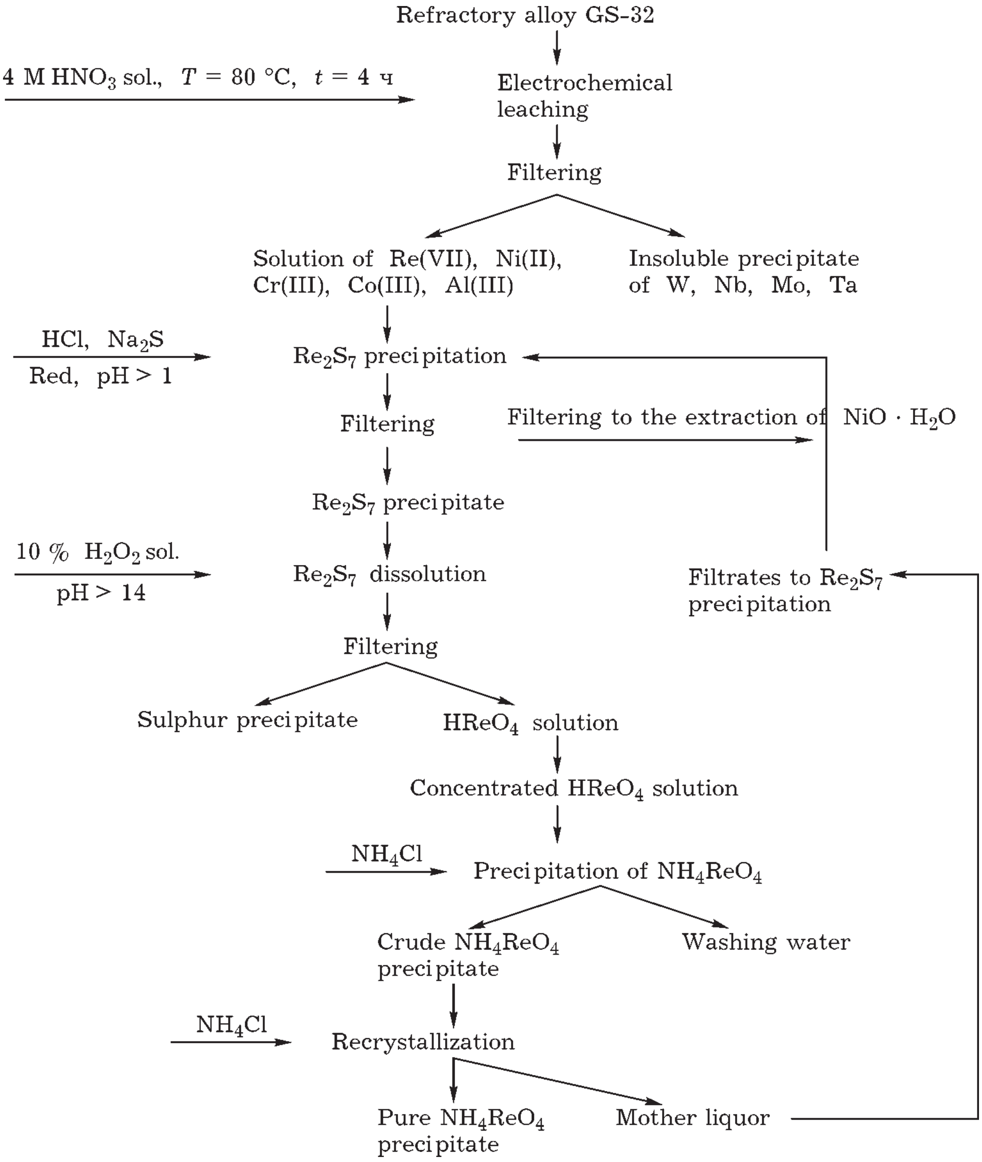

Fig. 1. Schematic diagram of the sulphide process for rhenium extraction.

sorbing. Then, the filtrate and the wash water is used for quantitatively recovering ReO_2 by means of reducing $[ReO_4]^-$ with the help of a weighed portion of $NaBH_4$ in a weakly acidic medium. This reaction of quantitative obtaining ReO_2 is performed in accordance with the conditions reported in [8] those provide high reaction rate, good filtration and a high purity of the resulting precipitate. The use of $NaBH_4$ in a twofold excess with respect to stoichiometry does not lead to any contamination of the product with boron owing to the reaction of subsequent hydrolysis thereof. However, it is necessary for the reduction reaction being carried out at pH 1. In the case when the preset acidity appears exceeded, the ReO_2 is able to dissolve to a considerable extent with the formation of $H_2[ReCl_6]$, which imparts the solution a specific greenish-brown colour.

Thus, as the result of using these methods, rhenium is extracted from the alloy in the form of NH_4ReO_4 that meets in the properties the requirements of engineering specifications TU 48-7-1–90, as well as a bulk concentrate of refractory metals (W, Mo, Ta and Nb) is obtained. The solution of $Ni(NO_3)_2$ of high concentration (~360 g/L) with the impurity of similar cobalt salt (~33 g/L) could be readily converted via alkalization into marketable $Ni(OH)_2$ that corresponds to the requirements of engineering specifications TU 48-3-63–90 according to the standard content of controlled impurities and thus it could be directed to the production of electrodes for alkaline accumulator cells. It should be noted that in order to achieve the quality indicators of the highest AR-0 grade NH_4ReO_4 it is necessary to perform some special operations. So, the content of Mo in the salt should not exceed 0.0005 mass %. In order to achieve such a level of purity it is required to carefully observe the two experimental conditions.

The first concerns maintaining the lowest possible concentration of nitric acid during the final phase of the alloy dissolution. This restriction promotes obtaining a significantly lower content of Mo, W, Nb and Ta impurities in the solution. The transition of the mentioned metal impurities into the insoluble residue observed in practice is associated with an abrupt dropping the solubility of complex acids thereof. For example, the concentration of H_2MoO_4 exhibits a decrease from 14.3 to 1 g/L when the concentration of HNO_3 varies from 6 to 0.3 mol/L. The acids derived from the other mentioned metals behave likewise.

The second relates to the specific conditions of Re_2S_7 synthesis. As it was noted, obtaining the Re_2S_7 is possible with the use of a whole series of sulphiding reagents in the solid or gaseous state. Meanwhile, it should be noted that for the analytical purposes the best reagent is thioacetamide, whose use does not lead either to the contamination of rhenium sulphide with elemental sulphur or to the misinterpretation of gravimetric analysis. Notwithstanding this fact, the $CH_3C(S)NH_2$ convenient in operation uses to be replaced by sodium sulphide [9], thereby the purification of Re occurs efficiently due to the formation of water-soluble Mo and W thiosalts in alkaline, neutral or slightly acidic chemical media.

In our opinion, the processes proposed those result in the formation of NH_4ReO_4 with the purity required, could compete with the currently used ion exchange technologies.

CONCLUSION

Thus, the development of novel methods for isolation and purification of rhenium from recycled materials with obtaining high-purity perrhenates would allow not only eliminating the deficiency thereof, but expanding to a considerable extent the modern scope of using this metal.

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