Recovery of tungsten, molybdenum, and tantalum from the semi-product of comprehensive processing of rhenium-containing nickel-based superalloys

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The relevance of the dissertation topic is driven by the growing demand of global and Russian industry for strategically important metals − tungsten, tantalum, molybdenum, and rhenium. Due to their high melting points, corrosion resistance, and mechanical strength, these metals are indispensable in the production of alloying additives for superalloys, tantalum electrolytic capacitors, cutting tools, and corrosion-resistant chemical equipment. These metals are key components of rhenium-containing nickel-based superalloys used in the aerospace and energy sectors for manufacturing turbine blades and disks in aircraft engines as well as stationary gas turbines.

Nickel-based superalloys contain 3–9 % rhenium, 4–9 % tungsten, 1–4 % tantalum, and 0.5–2 % molybdenum. According to FSUE «VIAM», 25–35 tons of waste are generated annually in Russia, a significant portion of which consists of lump scrap from gas turbine engine components and fine grinding sludge. Abroad (USA, Germany, Japan), the volumes of waste from rhenium-containing nickel superalloys are significantly higher. These wastes are processed using pyro- and hydrometallurgical as well as electrochemical methods, resulting in the accumulation of semi-products enriched in tungsten, tantalum, and molybdenum. Data on the recovery of these metals remain limited.

The advantage of developing processes for processing technogenic W-Mo-Ta semi-products lies in reducing the environmental impact and returning strategic metals to the production cycle. An additional incentive for organizing the processing of such wastes is the relatively small scale of production and, consequently, low capital costs.

Objective of the work − development of a technology for the extraction of tungsten, tantalum, and molybdenum from the semi-product of comprehensive

processing of rhenium-nickel superalloy waste with the production of marketable products.

Work objectives:

1. Establishment of the main regularities of sintering of the W-Mo-Ta-containing semi-product with alkaline reagents and determination of the optimal conditions for subsequent aqueous leaching of the sinters with sodium hydroxide and sodium carbonate.

2. Leaching of the pre-oxidized (in air) W-Mo-Ta semi-product with sodium hydroxide solutions and optimization of the process conditions.

3. Optimization of the conditions for selective precipitation of tungstic acid from the leaching solutions of the W-Mo-Ta semi-product sinters with alkaline reagents and recovery of molybdenum from the mother liquors using phosphorus-containing sorbents.

4. Determination of the conditions for hydrofluoric-sulfuric acid leaching of tantalum from the Ta-containing semi-product followed by testing of extraction, sorption, and precipitation methods for its recovery from the resulting solutions.

5. Preparation of an impregnate based on 1-octanol and determination of its sorption characteristics for the recovery of tantalum from the processing solution of the Ta-containing semi-product.

6. Development of a principal technological flowsheet for the extraction of tungsten, tantalum, and molybdenum from the W-Mo-Ta semi-product with the production of marketable products.

Scientific novelty:

1. It was established that the change in enthalpy during alkaline leaching of tungsten and molybdenum from the oxidized W-Mo-Ta semi-product in the temperature range of 40–120 °C amounts to −113.1 and −69.6 kJ/mol, the change in entropy is +109.7 and +50.3 J/(mol·K), and the change in Gibbs free energy ranges from −84.6 to −145.8 kJ/mol, respectively. The apparent activation energy of the process was determined to be 26.0±1.3 and 24.5±1.2 kJ/mol, respectively, confirming that the process is limited by the chemical reaction.

2. An increase in the sorption capacity for molybdenum on the binary TVEX sorbent D2EHPA+HPO was revealed due to a combined cation-exchange and solvation mechanism of molybdenyl ion extraction from hydrochloric acid mother liquors after tungstic acid precipitation. The capacity for molybdenum reaches 205 mg/g, which is 1.8 times higher than that achieved with TVEX–D2EHPA.

3. The rate constant for saturation of the styrene-divinylbenzene porous matrix with 1-octanol during the preparation of the impregnate was determined to be $(5.2\pm0.5)\cdot10^{-3}$ $min^{-0,5}$. The equilibrium capacity of this impregnate for tantalum sorption from sulfate-fluoride solution via the hydrate-solvate mechanism (confirmed by FTIR spectroscopy) reaches 440 mg/g.

Theoretical and practical significance of the work:

1. Optimal conditions for sintering of the W-Mo-Ta semi-product with alkaline reagents were determined.

2. The possibility of sorption recovery of molybdenum from the hydrochloric acid mother liquor after tungstic acid precipitation using TVEX sorbents containing organophosphorus extractants was demonstrated.

3. The possibility of extraction, precipitation, and sorption recovery of tantalum from the sulfate-fluoride solution obtained after leaching of the Ta-containing semi-product from comprehensive processing of rhenium-nickel superalloy waste was shown.

4. An impregnate based on 1-octanol was obtained with high capacity and kinetic characteristics (determined during composition optimization) for tantalum sorption from hydrofluoric-sulfuric acid media, offering improved fire and explosion safety compared to liquid-liquid extraction.

5. A principal technological flowsheet for the recovery of W, Ta, and Mo from the W-Mo-Ta-containing semi-product with the production of marketable products was developed and tested.

The novelty of the technical solution regarding the use of the 1-octanol-based impregnate for tantalum recovery is confirmed by the issuance of Russian Federation Patent No. 2835950 with priority date of July 15, 2024.

Provisions submitted for defense:

1. Regularities of sintering of the W-Mo-Ta-containing semi-product from comprehensive processing of rhenium-nickel superalloy waste with alkaline reagents and nitrogen-containing oxidants.

2. Regularities of leaching of the pre-oxidized W-Mo-Ta-containing semi-product from comprehensive processing of rhenium-nickel superalloy waste with sodium hydroxide solutions.

3. Sorption characteristics of TVEX sorbents for molybdenum recovery from the hydrochloric acid mother liquor after tungstic acid precipitation.

4. Capacity and kinetic characteristics of sorbents for tantalum recovery from sulfate-fluoride solutions obtained after leaching of the Ta-containing semi-product from comprehensive processing of rhenium-nickel superalloy waste. Sorption mechanism of tantalum on the 1-octanol impregnate (50 wt. %).

5. Principal technological flowsheet for processing of the W-Mo-Ta semi-product and results of pilot-scale laboratory tests.