RECYCLING OF TUNGSTEN FROM DIAMOND CORE DRILLING CROWNS

Silvana Dimitrijević [1], A. Ivanović, M.Bugarin [1], J. Petrović [1], S.P. Dimitrijević[2]

[1]Institute of Mining and Metallurgy Bor, [2]Innovation Center of the TMF Belgrade

Abstract

Diamond crowns used for research-geological drilling obtained by sintering particles of tungsten carbide and cobalt (hard metal) and iron with diamonds have a wide application in geology and mining. According to the research, the cost of cobalt and tungsten production from ores is four times higher than the cost of the recycling from hard metals. The paper describes the first phase of the recycling of diamond crowns and the production of tungsten in the form of sodium tungstate.

Keywords: Recycling; tungsten carbide; sodium tungstate;

Introduction

"Cement Carbides" of tungsten are widely used in the hard metal industry for the production of wear-resistant tools:

- cutting tools (50-60%),
- tools for drilling in mining and geology,
- matrices, nozzles and valves,
- tools for processing various metals and hard coatings.

Most cement carbides consist the powder of WC and Co in a general ratio of 70% to 97%, of the total mass, and the rest is a binding metal.

Introduction – importance of the recycling

- The most important primary raw materials of tungsten are minerals: wolframite ((Fe, Mn)WO4) and scheelite (CaWO4).
- However, rich deposits are rare and the process of obtaining is associated with major environmental problems whose solution is more expensive to produce.
- Waste materials with WC can be considered as significant secondary resources of tungsten and cobalt. This is especially important, because in the last ten years, the primary raw materials of tungsten have risen drastically (multiplied) and electricity costs (the main cost in W production) have grown by around 30% worldwide.
- **The production of tungsten through the recycling of waste hard metal reduces costs and energy consumption;**
  therefore has a positive economic and environmental impact.

Form of the WC waste and recycling methods

The share of produced W from recycling is increasing continuously, but even nowadays, **it has not yet exceeded 25%.**

This is a consequence of very different physical forms and the chemical composition of the waste material.

The waste material with WC classified according to the form in which it appears:

powder (soft waste); pieces (hard waste); defects in production (mostly HW).

Methods for the recycling of WC waste materials, can be divided into four groups:

1. hydrometallurgy,
2. pyrometallurgy (melting),
3. direct recycling and
4. semi-direct recycling.

Experimental

• The aim of the research in this paper was the recycling of tungsten from diamond core drilling crown in the form of sodium tungstate by leaching in nitric acid.

Figure 1. Diamond core drilling crown

Table 1. XRF analysis of diamond core drilling crown

Element (%)	*Sample 3*
W	55,96
Cu	23,39
Ni	6,16
Fe	13,48
Ti	0,22
P	<0,005

Results and discussion

Cu, Ni, and Fe are dissolved by following reactions:

$$Cu + 2HNO_3 \rightarrow Cu(NO)_3 + H_2O$$

$$Fe + 2HNO_3 \rightarrow Fe(NO)_3 + H_2O$$

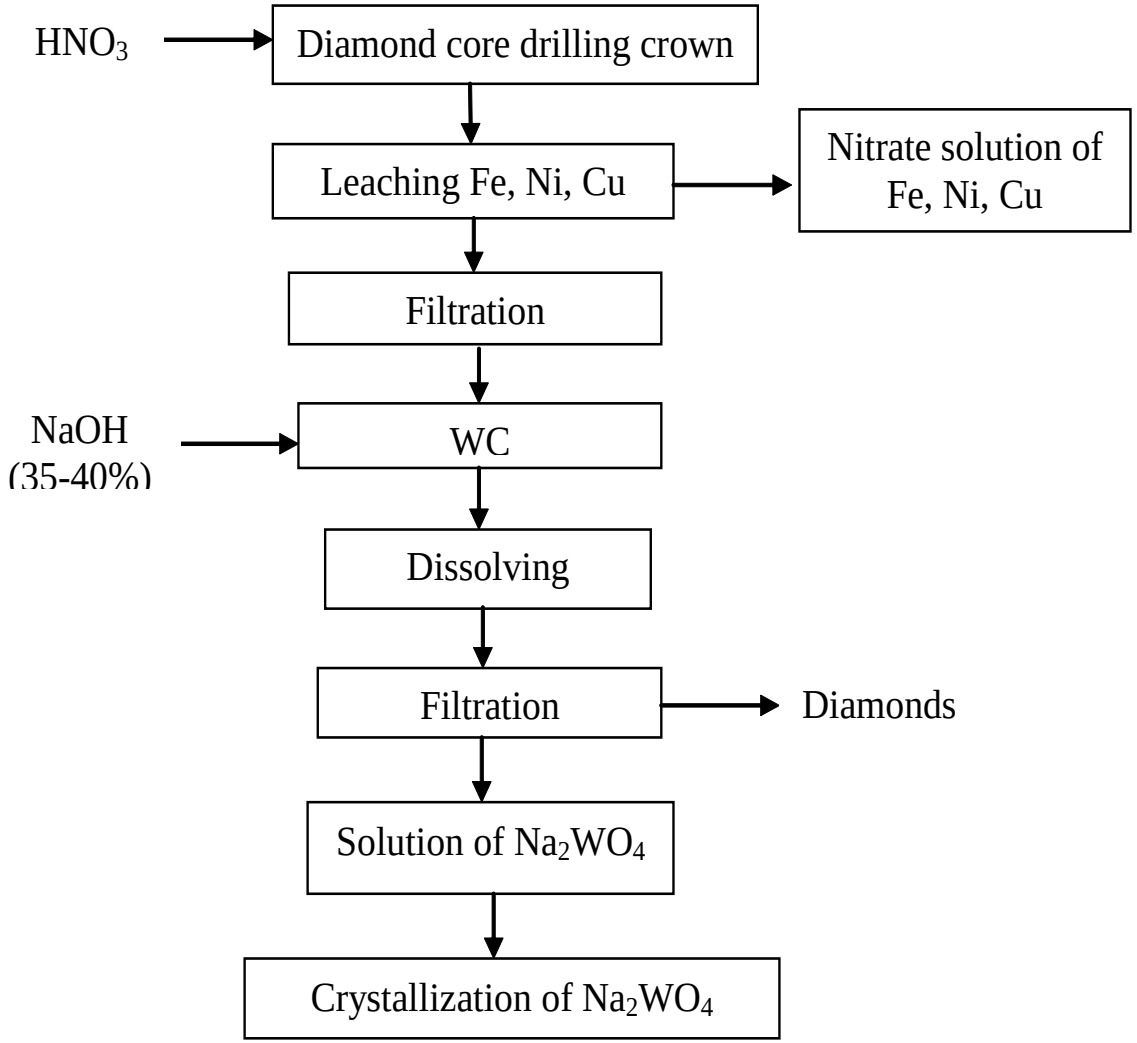
$$Ni + 2HNO_3 \rightarrow Ni(NO)_3 + H_2O$$

After leaching in nitric acid, WC as insoluble residue was dissolved with concentrated sodium hydroxide in order to obtain sodium tungstate by reaction:

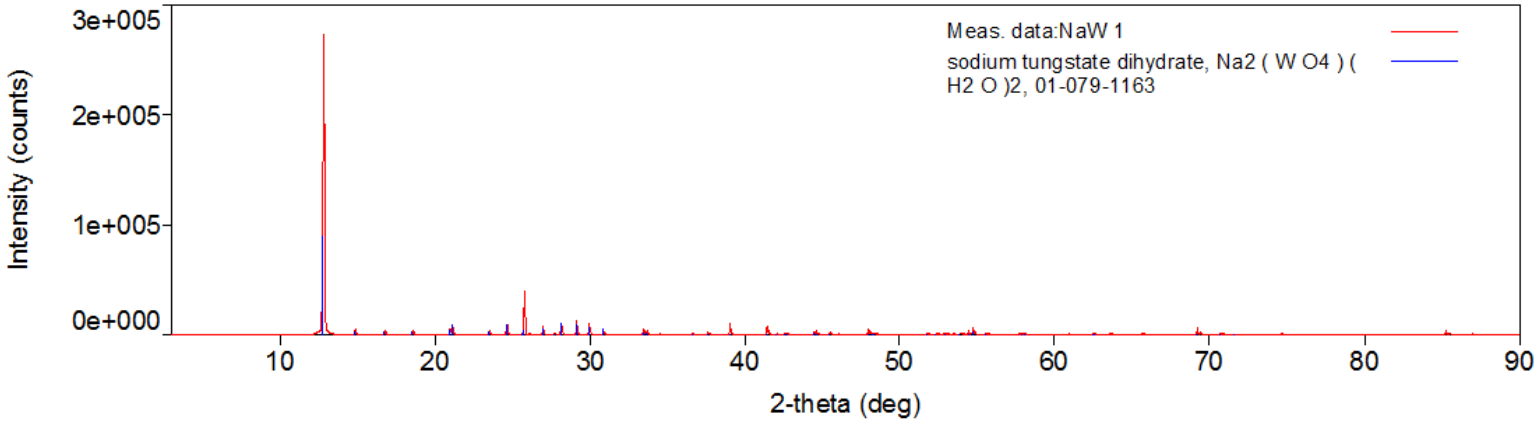
$$WC + 2NaOH + H_2O \rightarrow Na_2WO_4 + CO_2 + H_2$$

The degree of tungsten leaching of 98.58% was achieved. After filtration, the solution was evaporated at 90°C in order to crystallization sodium tungstate.

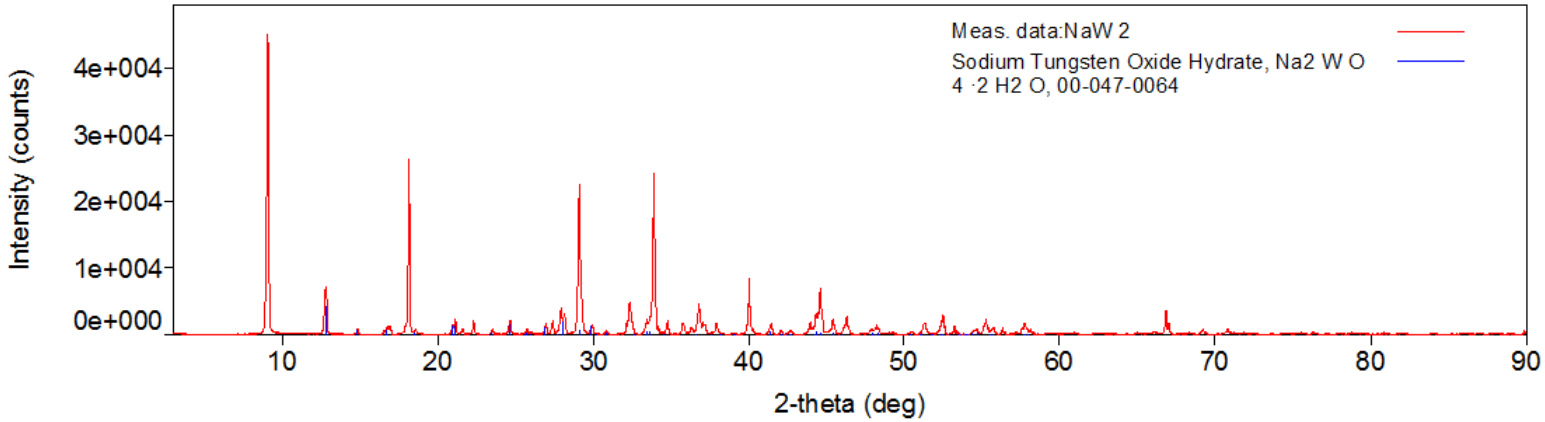
Technological scheme of leaching the diamond core drilling crown



X-ray diffractograms

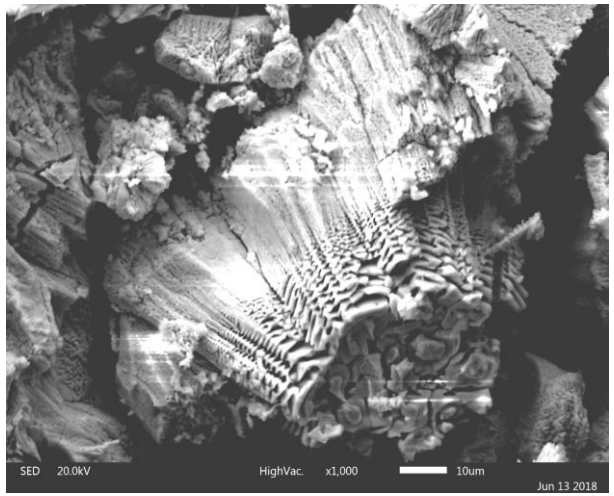


(a) sodium tungastate dihydrate (Commercial)

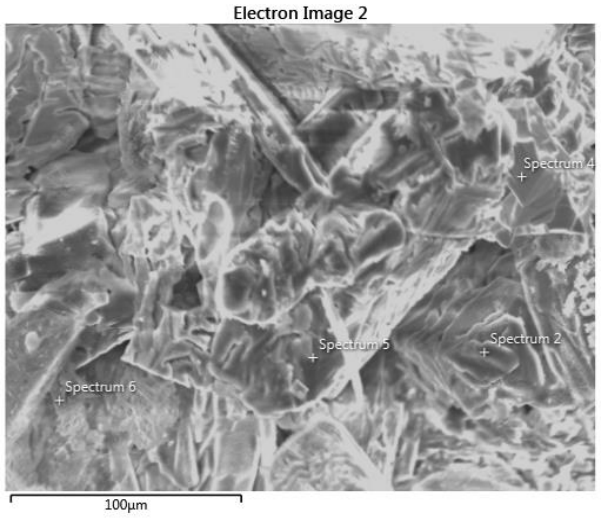


(b) sodium tungastate obtained by recycling

SEM and EDS analysis



SEM image of sodium tungastate dihydrate



Left:
EDS image (a)with EDS spectra (b-c) for sodium tungastate dihydrate obtained by recycling (EDS analysis given in Table 2)
Right:
Macrophotography of diamonds obtained by recycling

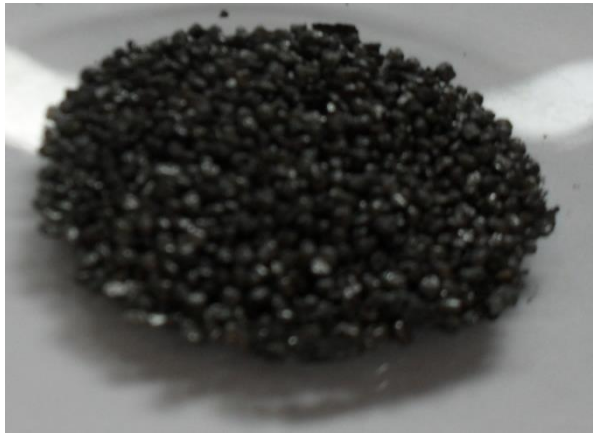


Table 2. EDS analysis of sodium tungastate dihydrate obtained by recycling

Element (%)	*O*	*Na*	*W*	*Σ*
Spectrum 2	40,94	23,78	35,24	100,00
Spectrum 4	22,25	16,85	60,90	100,00

Conclusion

- Based on laboratory research on the recycling of diamond crowns of drills, it can be concluded that the recycling costs: 3.2 € / kg of hard metal, or four times less compared to the cost of production of tungsten and cobalt from the ore.
- Diamonds are practically by-products (the most valuable) since they practically remain insoluble after recycling tungsten (in the form of sodium tungstate). Sodium tungstate obtained by the recycling process is of technical quality.

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Thank you for your attention!!