



Recycling of rhenium-containing wire scrap[☆]

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ABSTRACT

Rhenium is a refractory metal and is one of the rarest elements. Due to its high cost, recycling of rhenium-containing scraps is of economic interest. This paper pertains to the recycling of rhenium from tungsten–rhenium wire scrap generated in the manufacturing of W₉₇Re₃ wire. Rhenium from wire scrap, which contained 3.1–3.4% Re, was volatilized at 900 °C in the presence of air at 2 L/min in a tube furnace according to the following equation: $4\text{Re} + 7\text{O}_2 \rightarrow 2\text{Re}_2\text{O}_7$ (g). Volatilized Re was solidified on the inner surface of the tube and was recovered as ammonium perrhenate (NH₄ReO₄) solution after washing the tube with dilute ammonium hydroxide solution ($\text{Re}_2\text{O}_7 + 2\text{NH}_4\text{OH} \rightarrow 2\text{NH}_4\text{ReO}_4 + \text{H}_2\text{O}$). Ammonium perrhenate solution was crystallized to obtain ammonium perrhenate crystals which were free of tungsten and other metal impurities. First pass yield of rhenium recovery was 65.1%. Ammonium perrhenate crystals were reduced in hydrogen at 400–700 °C to obtain Re-metal powder: $(2\text{NH}_4\text{ReO}_4 + 7\text{H}_2 = 2\text{Re} + 8\text{H}_2\text{O} + 2\text{NH}_3)$. Rhenium metal powder obtained from the W–Re wire scrap was blended with non-sag tungsten powder to make a 6 kg W₉₇Re₃-alloy ingot which was rolled to make tungsten–rhenium wire. Results presented in this paper were intended for developing a commercial process for the recycling of a large inventory of W–Re wire scrap.

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1. Introduction

Rhenium is scarce in the earth's crust being present at <1 ppb [1,2]. Most of the Re-production comes from the flue gases during roasting of molybdenite concentrates. These concentrates are commonly found in porphyry ores of copper. Rhenium is considered a byproduct of copper mining. Major sources for rhenium are in Chile, Russia, Kazakhstan, Ukraine, and the southwestern United States.

Rhenium has many applications [3–7]. For example, it is used in small rocket thrusters to position satellites and help them maintain a geo-stationary orbit. Rhenium in the form of pellets is added to nickel-based super-alloys in order to raise the operating temperature of turbine blades in aircraft and gas turbine engines [4,5]. Rhenium is also used in medical applications such as in the prevention and treatment of restenosis as well as in the treatment of liver tumor(s) [4]. In other applications, rhenium is used in the petroleum industry as part of the bi-functional Pt–Re naphtha reforming catalyst [6,7].

Due to its high electrical resistance and low vapor pressure, rhenium is an excellent choice for filaments [4]. A major advantage of rhenium is that it imparts its good qualities to other metals. Therefore it is added to molybdenum and tungsten to improve their qualities especially ductility. Wires made of rhenium are used in photoflash lamps in photography, high temperature thermocouples, and thermistors. Tungsten–3%

rhenium wire is used for certain applications in lamps, electronic tubes, and other devices requiring W wire that re-crystallizes to a ductile state. In applications requiring elongation or resistance to shock and vibration, tungsten–3% rhenium wire is often superior to standard tungsten wire. Tungsten–3% rhenium heaters in radio tubes and cathode ray tubes remain ductile even after thousands of hours of operation.

Tungsten–rhenium wire production generates a significant amount of W–Re wire scrap which, as it is, cannot be re-cycled in the tungsten process. In addition, Re is a quite expensive metal and therefore recovery of Re from wire scrap is highly economic. After Re recovery, tungsten from oxidized wire (mainly tungsten oxide) could also be recovered.

Methods of Re recovery from W–Re wire scrap are reported in the literature [8–13], however none of the references reported recycling of the recovered Re in the manufacturing of W–Re wire. U.S. Patent No. 45213818 [8] describes the dissolution of W–Re wire scrap in a NaOH-fusion in the presence of oxidizing agents such as NaNO₃ and NaNO₂. The resulting fused material contained essentially all of the tungsten and rhenium in oxidized form as sodium tungstate and sodium perrhenate. The W–Re solution was treated with an anionic resin containing styrene divinylbenzene copolymer lattice with a relatively high degree of cross-linking to which quaternary ammonium exchange groups were attached. ReO₄[−] ions were retained by the resin and were separated from tungstate anions. ReO₄[−] was stripped from the resin with a stripping solution containing 25 gal of tributyl phosphate and about 6.88 gal of reagent grade 37%-hydrochloric acid. Finally Re was recovered as ammonium perrhenate solution from tributyl phosphate in the presence of ammonium hydroxide. No further treatment or crystallization of ammonium perrhenate solution was reported.

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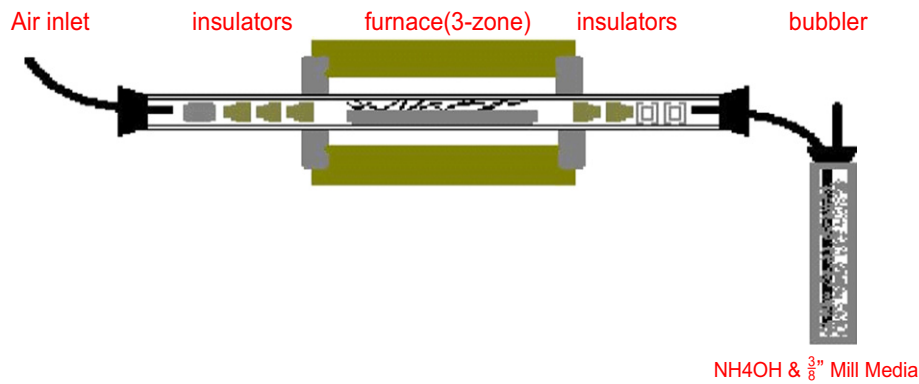


Fig. 1. Experimental set-up for sublimation.

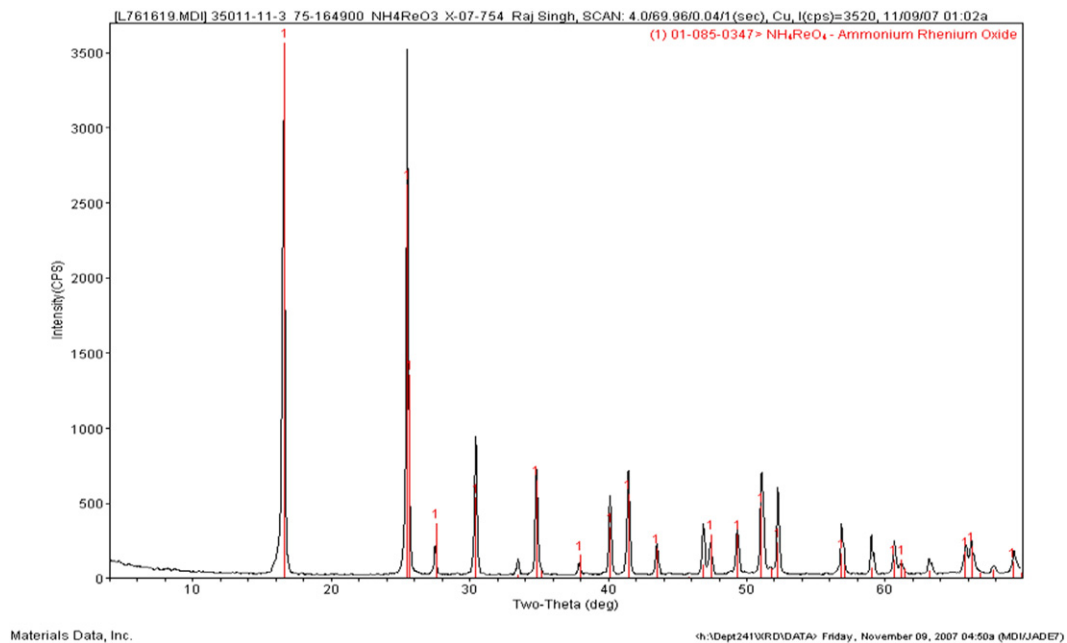


Fig. 2. XRD of the NH_4ReO_4 crystals made by Method-1.

U.S. Patents [9–12] reported the separation of Re and W from fused sodium perrhenate and sodium tungstate solutions using different ion exchange and precipitation methods. However, none of the patents reported crystallization and reduction of ammonium perrhenate to make Re metal powder. Moreover, all these methods seem to be capital intensive and use very strong alkali fusion to dissolve wire scrap.

U.S. Patent No. 4604265 [13] described a multi-step oxidation process of W–Re wire scrap involving firing the scrap in an oxidizing atmosphere at a sufficient temperature for a sufficient time to convert the tungsten and rhenium to their respective oxides. After the first pass, the scrap was ground and re-oxidized to improve over-all Re-recovery from the scrap. However no further treatment of oxides of rhenium was reported. Moreover, only three experiments were performed to volatilize Re from small amounts (50–100 g per experiment) of wire scrap.

The present paper also uses oxidation (volatilization) of Re from W–Re wire scrap to separate Re as ammonium perrhenate, however, the main aim of this work was to demonstrate the conversion of recovered Re to ammonium perrhenate crystals and their conversion to Re-metal powder for application in W–Re ingot making. In all 10 batches of 1.5 kg wire scrap were performed to volatilize Re which was converted to ammonium perrhenate by evaporative crystallization. Ammonium perrhenate was reduced in hydrogen to make Re metal powder.

About 300 g Re powder, sufficient for characterization and 6 kg W_{97}Re_3 -alloy ingot making was made. The work was intending to develop an industrial process to recycle a large inventory of W–Re wire scrap.

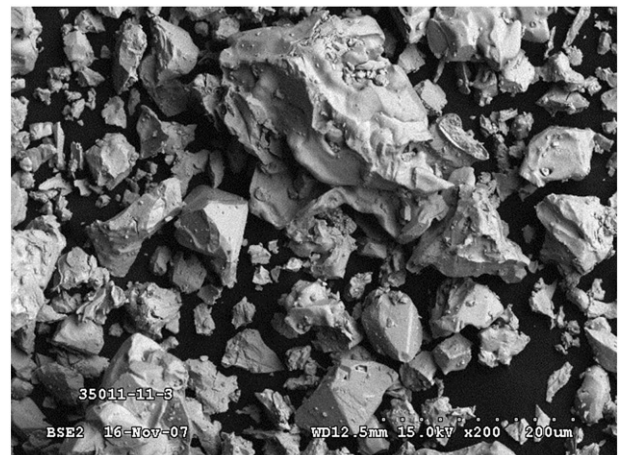


Fig. 3. SEM of NH_4ReO_4 crystals made by Method-1.

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