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Production of high-purity ammonium perrhenate for W–Re–Ni–Fe heavy alloys

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ABSTRACT

The paper presents the developed method for purification of ammonium perrhenate solutions by ion-exchange method on strongly acidic cation-exchange resin C160. The developed method is characterized by high, over 95% efficiency of sorption of potassium, sodium, calcium, iron, magnesium and lead ions, and high efficiency of regeneration of the resin with 32% solution of nitric(V) acid. In that way ammonium perrhenate was produced of the following composition: 69.4% Re, <0.0005% Ca, <0.001% K, <0.0005% Mg, <0.0005% Cu, <0.0005% Na, <0.0005% Mo, <0.0005% Ni, <0.0005% Pb, <0.0005% Fe. Some selected results of the experiments into possibilities for application of that specifically purified ammonium perrhenate in production of W–Re–Ni–Fe heavy alloys are presented as well as physical and mechanical properties of the heavy alloys. It was established that the purified ammonium perrhenate is a proper material for production of heavy alloys, and the generated sinters can be used in manufacture of armour-piercing discarding sabots.

1. Introduction

In the solid state rhenium is a ductile metal of significant hardness, high melting point (3453 K) and density (21.0 g/mL) [1–3]. Because of its specific properties one of the areas of its application is in production of tungsten-based heavy alloys. The significance of that metal in its alloys with tungsten and molybdenum results from so called “rhenium effect” [4,5]. Introduction of rhenium into tungsten during alloy formation brings: advantageous change of composition and form of tungsten oxides, reorganization of oxides and carbides in the alloy microstructure and change in mechanism of material deformation. In the result the tungsten oxides, similar to the oxides in the alloys of molybdenum with rhenium, take a complex form of spherical shape and are distributed throughout the whole volume of the alloy (also inside particles of high-melting phase). Rhenium presence in heavy alloys makes them applicable to manufacture of specific products, e.g. in aircraft and armament industry, and of thermoelements, catalysts and some electric contacts [6,7]. One of specific applications of heavy alloys with rhenium addition is in production of the cores of armour-piercing discarding sabots [8,9]. The Military University of Technology in Poland (WAT) has been running studies into application of rhenium as alloy addition in heavy alloys for many years already. In the beginning metallic rhenium powders and high purity ammonium perrhenate made by Aldrich were used for that purpose. This study shows possibilities for their substitution with ammonium perrhenate (APR), produced from APR manufactured by KGHM Polska Miedź S.A., Polish producer of electrolytic copper, specifically purified by ion-exchange technique [10]. The necessity for the purification results from presence of potassium which has adverse influence on mechanical properties of a sinter. Potassium becomes oxidised during reduction in a furnace and collects on the surface of metallic rhenium grains in a form of oxide which changes properties of the sinter [11].

Many technologies are used worldwide for production of APR from primary and secondary materials. Many grades of APR are available on the market, different in purity and range of analyzed impurities. The most common and most universal method for purification is based on recrystallization from water, however that method shows significant limitations in removal of potassium. Majority of perrhenates, e.g.: of calcium, sodium, magnesium, iron, nickel and cobalt, have higher solubility in water than APR while potassium perrhenate shows low solubility in water, significantly lower than ammonium perrhenate, therefore it is difficult to remove it by recrystallization from water [12,13].

This article presents a method for production of high purity APR which can be used as a source of rhenium for production of W–Re–Ni–Fe alloys.

2. Experimental

2.1. Materials

Studies into ammonium perrhenate purification were conducted with selected strongly acidic cation-exchange resins in a hydrogen form: C150, C160,

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SGC650 – by Purolite; S100, SP112 – by Lanxess; Marathon MSC – by Dow Chemicals and Amberlite252, Amberjet1600 – by Rohm and Hass. In the study Polish crude APR was used, which contained about 69% Re and 0.002% Ca, Mg and Fe, 0.003% Na, 0.001% Pb and 0.0017–0.05% K. The following reagents were applied: nitric(V) acid, sulfuric(VI) acid, ammonia solution and aqueous solution of hydrogen peroxide. The reagents were made by POCh, Gliwice and p.a. grade. Redistilled water was used in all the studies, of conductivity < 2 μS/cm. For comparison ammonium perrhenate made by Aldrich (No. 316954) was also used in the studies into production of sintered W–Re–Ni–Fe heavy alloys.

2.2. Analytical methods

All the analyses into APR purification were performed in the certified Analytical Chemistry Department of IMN. In determination of rhenium content in APR a gravimetric method was used, while the analysis of impurities, i.e. determination of K, Ca, Ni, Fe, Cu, Mg, Na, Mo and Pb contents, was performed by atomic emission spectrometry with inductively coupled plasma in Horizon ARL ICP-OES equipment.

2.3. Studies into ammonium perrhenate purification

This part of the study shows results of ammonium perrhenate purification from cation (mainly potassium) impurities. Ion-exchange method with sorption on strongly acid cation-exchangers was used for their removal from aqueous NH_4ReO_4 solutions.

2.3.1. Cation-exchanger selection – static conditions

A batch of 300 mL of 10% H_2SO_4 was added to the selected cation exchanger of 20 g mass (with exception of C160 ion-exchanger in which conditioning was done with 10% sulfuric(VI) acid and with 32% nitric(V) acid) and then mixed for 1 h. After conditioning the ion-exchanger was washed with water until pH of 7 was reached in the washings. Ammonium perrhenate solution was made by dissolving 25 g of NH_4ReO_4, which contained: 0.002% Ca, 0.026% K, 0.002% Mg, 0.003% Na, 0.002% Fe, 0.001% Pb, in 1 L of water. The produced solution of pH 5 was mixed with a batch of ion-exchanger at room temperature for 1 h. Once the ion-exchange reaction was finished the resin was separated from the solution by filtration and the filtrate was neutralized with 25% solution of aqua ammonia, where 100 mL of NH_{3aq} was used for each 1 L of the solution. The neutralized solution was vaporized until dry in the temperature of 353–373 K under pressure of 0.03–0.05 MPa. During evaporation 25% ammonia solution was added in the amount necessary to maintain pH at the level not lower than 9. The produced solid, crystalline ammonium perrhenate was washed with 50 mL of 15% aqueous solution of hydrogen peroxide (cooled down below 278 K). Thus received ammonium perrhenate was dried in the temperature of 383 K, and then analyzed to determine the content of rhenium and selected impurities, i.e.: potassium, magnesium, calcium, lead, iron and sodium. In every test the efficiency of sorption of individual metal ions (W_x) was calculated in %:

$$W_x = \frac{m_x - C_x V}{m_x} \times 100 \qquad (1)$$

where

- m_x is the mass of the metal in initial solution [g],
- C_x is the metal concentration in the solution after sorption [g/L],
- V is the volume of the solution after sorption [L].

2.3.2. Purification of aqueous solutions of ammonium perrhenate by C160 cation-exchanger – static conditions

2.3.2.1. Selection of ion-exchanger amount. The study was conducted in the same conditions as described in Section 2.3.1, at various masses of ion-exchangers (5–25 g).

2.3.2.2. Potassium content in ammonium perrhenate. Next investigations focused on examination of the influence of potassium content in ammonium perrhenate (0.05, 0.026, 0.005, 0.003 and 0.0017%) on the degree of its purification. Also here the conditions were the same as described in Section 2.3.1.

2.3.3. Studies into purification of ammonium perrhenate on large laboratory scale – dynamic conditions

Investigations into purification in dynamic conditions were conducted with 800 g (1000 mL) of C160 ion-exchanger. The ion-exchanger was conditioned in static conditions by application of 2000 mL of 32% nitric(V) acid for 1 L of ion-exchanger. The conditioning was carried out for 2 h and then the cation-exchanger was washed out of acid by decantation (until pH 7 was reached) and placed in ionic column of diameter 0.05 m. In the next step 250 g of ammonium perrhenate (of potassium content 0.026%) was dissolved in 10 L of water to produce NH_4ReO_4 solution of concentration 25 g/L, pH 5 and of the following composition: 1.68 g/L NH_4^+, 17.35 g/L Re, 0.065 g/L K. The solution was run through the column at the rate of 2 L/h from the top to the bottom. The sorption was conducted in room temperature until pH of the effluent was ≤2. In the next step the ion-exchanger was washed with 3 L of water in the direction opposite to the sorption. The effluent from sorption was collected in equal batches, 1 L each. After pH measurement each part of the effluent was separately treated, i.e. neutralized with 25% solution of aqua ammonia, using about 100 mL of 25% NH_{3aq} for 1 L of solution. The neutralized solution was concentrated in the rotary vacuum evaporator under conditions described in Section 2.3.1. Thus produced ammonium perrhenate was analyzed to determine its potassium, sodium, magnesium and calcium contents. The results were used to calculate sorption parameters as defined in Section 2.3.1. At the end of the task the whole volume of the produced crystalline APR was combined and analyzed to determine content of rhenium and nine basic impurities, i.e.: K, Na, Cu, Fe, Pb, Ca, Mg, Mo and Ni.

2.3.4. Studies into purification of ammonium perrhenate from potassium on large laboratory scale – cyclic test

Within the scope of the study 25 cycles of C160 cation-exchanger operation were examined, where each cycle consisted of: sorption, washing of cation-exchanger out of sorption solution, regeneration of cation-exchange bed – elution of the ions bound on the ion-exchanger and washing of the cation-exchanger out of regenerating agent. The conditioning, washing of the cation-exchanger after conditioning and sorption were conducted in the same conditions as described in Section 2.3.3. Washing after sorption was performed with water in the direction opposite to the flow of sorption solution (i.e. from the bottom to the top). In that way 3 L of water was run through the bed. The solution after sorption (of pH ≤ 1) and the washings were treated together, i.e. they were neutralized with 25% solution of aqua ammonia, using about 100 mL of 25% NH_{3aq} per 1 L of solution. The neutralized solution was vaporized until dry in the conditions described in Section 2.3.1, and the produced NH_4ReO_4 was washed and dried. The resin after washing was sent to regeneration – with volumetric proportions of ion-exchanger to the regenerating agent of 1:1.5 and with regenerating agent flow of 0.5 L/h. Effluent from the column was collected every 300 mL and its potassium content was determined. Washing of the ion-exchanger after regeneration was performed in two steps: in the first water in the volume four times higher than the bed volume was run at the rate of 4 L/h from the bottom to the top; and in the next water was run in the sorption direction in the volume necessary for the pH of effluent to reach 7. The resin after complete washing was used in the next sorption stage. Linear velocity of the purified solution was 2.2×10^{-3} m/s, while the velocity of regenerating agent (32% nitric(V) acid) was 5.5×10^{-4} m/s. The linear velocities of the solution flow were selected basing on the recommendations of resin manufacturer. In all the tests efficiency of potassium sorption were calculated according to Section 2.3.1, and efficiency of regeneration of the ion-exchanger out of potassium according to the following equation:

$$W_x = \frac{C_K V}{m''_K} \times 100\% \qquad (2)$$

where

m''_K is the mass of potassium ions absorbed on the ion-exchanger, defined as difference of the mass contained in the feed to the column and in the effluent from the column [g],
C_K is the potassium concentration in the solution after regeneration [g/L],
V_R is the volume of the solution after regeneration [L].

2.4. Production of W–Re–Ni–Fe alloys and examination of their properties

In the developed and used-in WAT method for production of sintered W–Re–Ni–Fe heavy alloys the metallic powders of tungsten, nickel, iron and rhenium were used as initial material. As an alternative ammonium perrhenate made by Aldrich (No. 316954) and produced specifically for that purpose at IMN was used in place of rhenium. Powder mixtures of compositions corresponding to the final compositions of the alloys with addition of 3, 5 and 10 wt% of rhenium were prepared by mixing powders in a planetary ball mill. The prepared mixtures were dried in a vacuum drier. The compacts in a form of rods of diameter 18 mm and length 0.025 m were prepared by cold isostatic pressing (CIP) under pressure of 300 MPa, with National Forge press. Sintering of compacts was done in two steps. Preliminary sintering in solid phase was conducted in a laboratory tubular furnace in the atmosphere of dissociated NH_3 (75% H_2 + 25% N_2). In the first sintering period in the temperature range between 873 and 1173 K, reduction of APR in the compacts took place. Also oxide coatings on the surface and inside particles of metal powders were reduced. The fundamental stage of that sintering operation was conducted in the temperature of 1423 K for 1 h, and then the compacts were cooled down in the furnace cooler to ambient temperature. Final sintering was performed in a SECO/WARWICK horizontal vacuum furnace 2.0 VP-4036/36 HV in the temperature of 1793 K, also for 1 h. Cooling of the sinters to the temperature of 1693 K was done at the rate of 5 K/min. Further cooling was performed at the rate of 15 K/min. During sintering the vacuum was at the level of 10^{-2} hPa, and in the cooling below temperature of 1693 K it was 10^{-3} hPa. After sintering all the rods were heat treated by solutioning and then standard samples for examination of physical and mechanical properties were made. The following parameters were determined in the examination of physical and mechanical properties of the produced sinters: density, porosity, yield point, tensile strength, elongation, hardness and impact resistance.

Table 1
Results of ion-exchanger selection for studies into NH_4ReO_4 solution purification.

Ion-exchanger	Mass of NH_4ReO_4 after purification g	Content in purified NH_4ReO_4, %						Sorption efficiency %	
		K	Ca	Mg	Na	Pb	Fe	K	Na
C150	24.1	0.005	<0.0005		0.001	<0.0005		80.1	65.4
C160	24.5	0.0035	<0.0005		0.0007	<0.0005		86.3	76.2
C160[a]	24.9	<0.001	<0.0005		<0.0005	<0.0005		>96.1	>83.3
S100	24.0	0.024	<0.0005		0.001	<0.0005		90.4	65.3
SP112	24.1	0.048	<0.0005		0.001	<0.0005		80.8	65.4
SGC650	24.5	0.052	<0.0005		<0.0005	<0.0005		79.6	<83.0
CT 275	24.6	0.025	<0.0005		<0.0005	<0.0005		90.2	>83.1
Amberlite252	24.5	0.048	<0.0005		0.001	<0.0005		81.2	66.0
Amberjet1600	24.4	0.036	<0.0005		<0.0005	<0.0005		85.8	>82.9
MarathonMSC	24.4	0.048	<0.0005		0.001	<0.0005		81.1	65.8

[a] Conditioning: 32% nitric(V) acid.

3. Results and discussion

3.1. Results of studies into purification of ammonium perrhenate

3.1.1. Selection of ion-exchanger

The highest, from among the tested ion-exchangers, efficiency of potassium sorption in the experimental conditions was observed with C160, which was, importantly in this case, conditioned in 32% nitric(V) acid. The efficiency was 96%. That ion-exchanger showed also high efficiency of sorption of other metals, i.e. sodium, magnesium, calcium, iron and lead. The other tested cation-exchangers also had high efficiency of magnesium, calcium, iron and lead sorption, however their sorption of sodium and, above all, potassium was lower which eliminated them from further tests, Table 1.

3.1.2. Purification of aqueous solutions of ammonium perrhenate with C160 cation-exchanger, in static conditions

3.1.2.1. Influence of phase ratio. It was observed that with the increase of ion-exchanger to solution ratio also efficiency of potassium and sodium sorption increases, while the efficiencies of magnesium, calcium, iron and lead sorption in the examined conditions were continuously high, each of them above 95%. Therefore it was decided that to remove sodium, magnesium, calcium, iron and lead to the level below 0.0005% and potassium below 0.001% from 1 L of solution of the following composition: 1.68 g/L of ammonium ions, 17.35 g/L Re, 0.065 g/L K, 0.0005 g/L Mg, Ca, Fe, 0.00075 g/L Na and 0.00025 g/L Pb, it is sufficient to use 20 g batch of C160 ion-exchanger (Table 2.).

3.1.2.2. Influence of potassium content in ammonium perrhenate on the degree of its purification. The studies have shown that in the examined conditions it is possible to reduce potassium content in NH_4ReO_4 to the expected level (<0.001% K) by sorption of potassium ions on C160 ion-exchanger even if its content is at the level of 0.5%. Also other cationic components of the solution were removed with high efficiency, which resulted in reaching the required level below 0.0005% for each component.

3.1.3. Purification of ammonium perrhenate in large laboratory scale – dynamic conditions

Results of the studies into purification of ammonium perrhenate in large laboratory scale confirmed efficiency of the selected method in removal of cationic impurities from aqueous solution of ammonium perrhenate. 240.7 g of ammonium perrhenate, of the following composition: 69.4% Re, <0.0005% Ca, <0.001% K, <0.0005% Mg, <0.0005% Cu, <0.0005% Na, <0.0005% Mo, <0.0005% Ni, <0.0005% Pb, <0.0005% Fe was produced from 250 g of the raw material. Purified at satisfactory level from potassium (<0.001% K) NH_4ReO_4 can be produced when solutions of $pH \leq 1$ are sent for neutralization and vaporization. That shows possibilities for controlling sorption process and precisely define its finishing moment, basing on the pH of effluent.

3.1.4. Purification of ammonium perrhenate in large laboratory scale – cyclic test

The developed method for purification of ammonium perrhenate from cationic impurities by sorption of cations on C160 ion-exchanger proved to be very efficient. In each of the examined cycles of ion-exchanger operation potassium sorption efficiency was high and exceeded 95%. Also efficiencies of potassium regeneration from ion-exchanger were high, in the range from 99.5 to 80.9%. In that case, however, gradual decrease of that parameter in the subsequent cycles was observed (Fig. 1). In the applied sorption and regeneration conditions it was possible to produce ammonium perrhenate of the following composition: 69.4% Re, <0.0005% Ca, <0.001% K, <0.0005% Mg, <0.0005% Cu, <0.0005% Na, <0.0005% Mo, <0.0005% Ni, <0.0005% Pb, <0.0005% Fe in twenty one cycles of ion-exchanger operation. Even though in the final four cycles potassium content was above the expected – permissible level it did not exceed 0.0013%. To generate 20 kg of ammonium perrhenate with K content <0.001%, which was then applied in production of tungsten-based heavy alloys, 4 L of C160 resin was used. Fig. 2 shows technological flow-sheet of the developed method. Thus produced APR was used in studies into production of tungsten-based heavy alloys for armour-piercing ammunition.

3.2. Description of methods for manufacture of W–Re–Ni–Fe and examination of their properties

Table 3 shows selected physical and mechanical properties of the produced W–Re–Ni–Fe alloys and (for comparison) respective results of examination of classical heavy alloy of composition 90W–7Ni–3Fe. It can be seen that the properties of the heavy alloys produced with specifically purified ammonium perrhenate are comparable to the properties of the materials in which commercial ammonium perrhenate made by Aldrich company was used as a source of rhenium. Analysis of porosity of the rhenium containing sinters shows that theoretical density was not reached and value of that parameter decreased with rhenium content increase. It seems important, however, that introduction of rhenium in a form of metallic powder to the sinter of the composition 87W–3Re–7Ni–3Fe results in lower density when compared to the materials in which ammonium perrhenate was used as rhenium source. Microstructure of heavy alloys is presented in Fig. 3. The first image shows a classical sinter of composition 90W–7Ni–Fe while in the second and the third, of respective compositions 87W–3Re–7Ni–3Fe and 80W–10Re–7Ni–3Fe, Re comes from ammonium perrhenate produced by the described method.

Table 2
Results of the studies into determination of C160 ion-exchanger mass for NH_4ReO_4 solution purification.

Mass of ion-exchanger, g	Mass of purified NH_4ReO_4, g	Content in purified NH_4ReO_4, %						Potassium sorption efficiency, %
		K	Ca	Mg	Na	Pb	Fe	
5	24.7	0.0024	<0.0005	<0.0005	0.001	<0.0005	<0.0005	7.7
10	24.7	0.0018	<0.0005	<0.0005	0.0008	<0.0005	<0.0005	30.8
15	24.8	0.0012	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	95.4
20	24.9	<0.001	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	>96.2
25	24.9	<0.001	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	>96.2

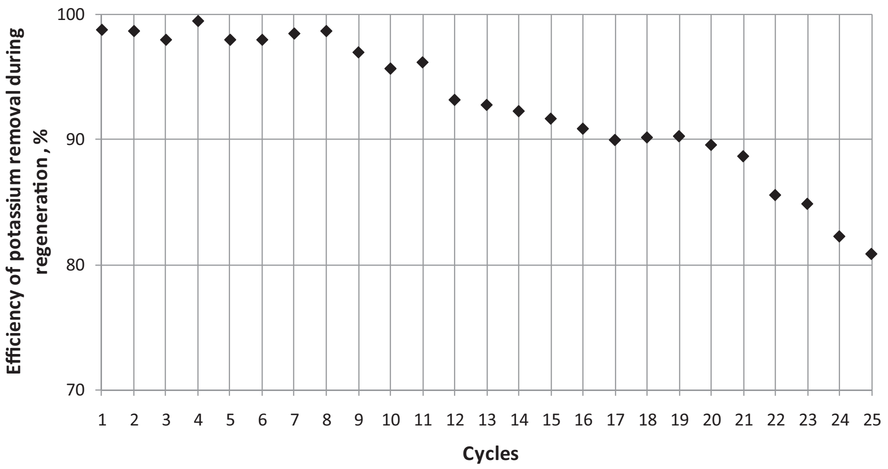

Fig. 1. Efficiency of potassium removal during regeneration in subsequent cycles.

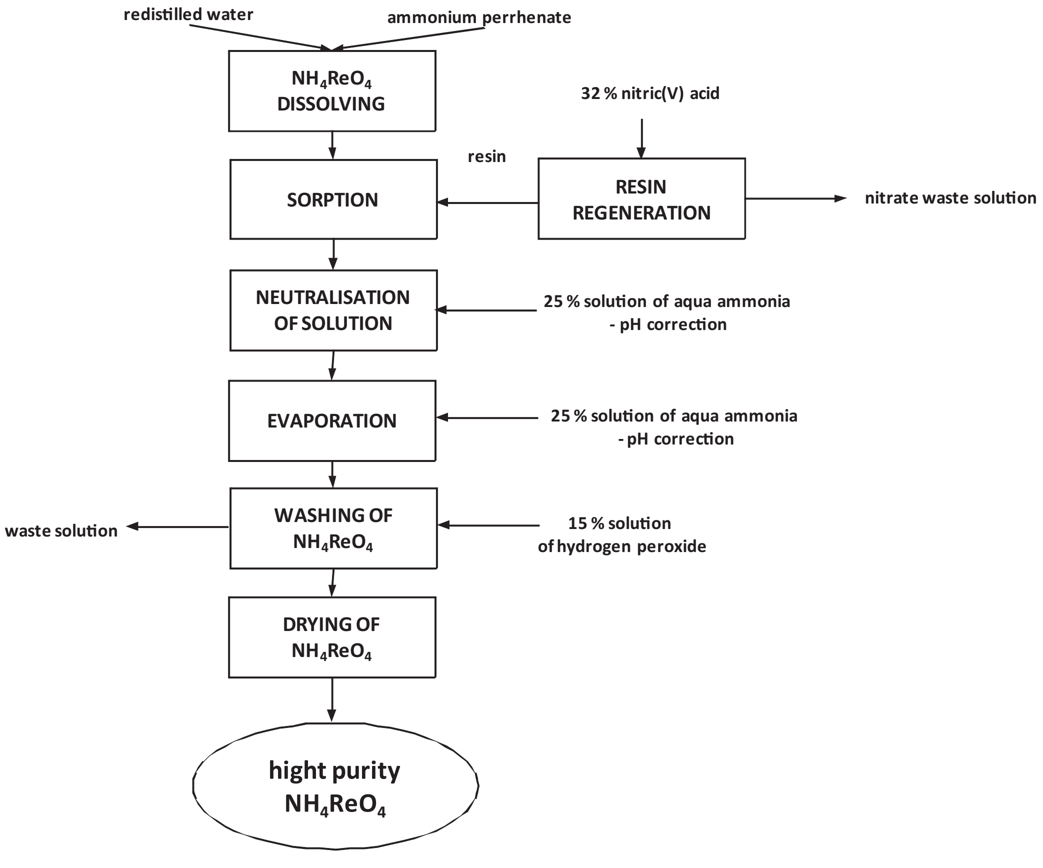

Fig. 2. Flow-sheet of the developed method for purification of ammonium perrhenate.

Table 3
Selected physical and mechanical properties of sintered W–Ni–Fe and W–Re–Ni–Fe heavy alloys.

Chemical composition and type of sintered material	Density, g/mL	Porosity, %	Yield point, MPa	Tensile strength, MPa	Elongation, %	Hardness HV5	Impact resistance, J/cm^2
90W–7Ni–3Fe	17.15	0	685	940	30	335	185
87W–3Re–7Ni–3Fe Re-metallic powder	17.01	1.50	970	1021	9.1	420	52.5
87W–3Re–7Ni–3Fe NH_4ReO_4 Aldrich	17.10	0.81	842	1150	18.7	373	96.7
85W–5Re–7Ni–3Fe NH_4ReO_4 USA	17.13	0.81	986	1189	7.0	350	65
80W–10Re–7Ni–3Fe NH_4ReO_4 Aldrich	17.05	1.61	1087	1192	6.1	448	40.7
87W–3Re–7Ni–3Fe NH_4ReO_4 IMN	17.12	0.69	760	1085	20	340	92
85W–5Re–7Ni–3Fe NH_4ReO_4 IMN	17.14	0.75	941	1130	6.0	347	76
80W–10Re–7Ni–3Fe NH_4ReO_4 IMN	17.12	1.21	1074	1185	7.0	440	37

It can be seen that microstructure of the sinters is similar, the images show matrix particles surrounded by bonding phase. The difference lies in various sizes and chemical composition of high-melting phase particles. In the classical heavy alloys the matrix is usually made of tungsten, while in the other two it is made of tungsten and rhenium alloy. Increase of rhenium content has significant influence on the size of matrix particles and results in their size reduction. It also increases their hardness, which brings increase of hardness of the whole material.

4. Conclusions

A method for production of high purity ammonium perrhenate of low potassium content (<0.001 ppm) was developed in IMN. Ion-exchange on strongly acidic cation-exchanger was used for NH_4ReO_4 purification. Several cation-exchangers were tested within the scope of the study. Influence of various parameters and factors on purification efficiency was thoroughly examined. It was found out that the most efficient NH_4ReO_4 purification takes place when C160 cation-exchanger, conditioned in 32% solution of nitric(V) acid, was used. The research results were confirmed in dynamic conditions in large laboratory scale. In the result of purification the aqueous solution was produced which contained NH_4ReO_4 and $HReO_4$, finally neutralized with ammonia solution and vaporized until dry in temperature 353–373 K, under pressure 0.03–0.05 MPa. In that way ammonium perrhenate was produced of the following composition: 69.4% Re, <0.0005% Ca, <0.001% K, <0.0005% Mg, <0.0005% Cu, <0.0005% Na, <0.0005% Mo, <0.0005% Ni, <0.0005% Pb, <0.0005% Fe. Also conditions of regeneration (with 32% nitric(V) acid) and ionic column washing (with water) were

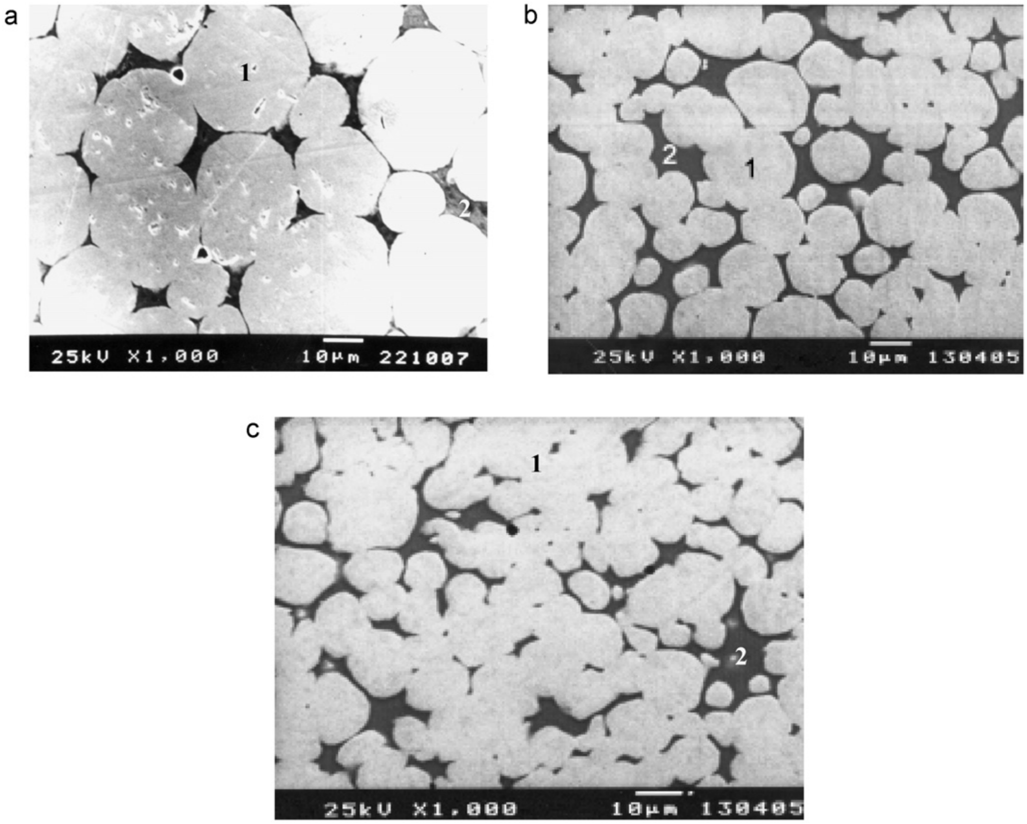

Fig. 3. Microstructure of heavy alloys: (a) 90W–7Ni–Fe, (b) 87W–3Re–7Ni–3Fe, (c) 80W–10Re–7Ni–3Fe; (1) high-melting phase (matrix), (2) bonding phase.

developed. The ammonium perrhenate free from potassium was used in production of W–Re–Ni–Fe heavy alloys. After examination and comparison of physical and mechanical properties (density, porosity, yield point, tensile strength, elongation, hardness and impact resistance) of the produced powders of W–Re–Ni–Fe heavy alloys with addition of ammonium perrhenate produced at IMN and purchased from Aldrich it was found out that the produced in IMN ammonium perrhenate represents a rhenium compound of appropriate purity to be used in production of heavy alloys.

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