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(56) Documents Cited:
WO 2013/063772 A1 **WO 2005/063382 A1**
CN 103193928 A **CN 101864033 A**
KR 100089621 A

(58) Field of Search:
INT CL **B01D, B01J, C01G, C08J**
Other: **EPODOC, WPI, TXTE, CAS-ONLINE**

(54) Title of the Invention: **Metals recovery method and polymer for use in metals re-covery and process for making such a polymer**
Abstract Title: **A process for forming a porous polymer template material and a method for its use in selective metal recovery.**

(57) A process of forming a porous polymer template material comprising polymerising a monomer admixed with a compound of the metal to be recovered, followed by treatment of the polymer to remove the metal compound. The metal to be recovered may be rhenium and the metal compound ammonium perrhenate. The polymer may be formed by cross-linking a monomer, such as vinylpyridine, in the presence of a porogen, such as chloroform, and a metal salt. The metal can then be removed by treatment with acid to give the polymer template material. Once formed the polymer template may be comminuted. A method of selectively recovering a metal from a solution containing the metal ions comprises contacting the aforementioned porous polymer template material with the solution containing the metal ions, and recovering the metal from the polymer by treatment with hydrochloric acid.

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METALS RECOVERY METHOD AND POLYMER FOR USE IN METALS RECOVERY AND PROCESS FOR MAKING SUCH A POLYMER

Field of the Invention

This invention relates to a method of recovering high-value metals such as rhenium from superalloys, a process for making a polymer for use in a metals recovery method, and a polymer adapted for such use.

Background to the Invention

Superalloys are metallic materials with a basic composition of nickel and cobalt or nickel and iron which, combined with other metals, form a highly resistant material. Use of metals such as rhenium in superalloys confers extraordinary properties to these alloys, such as increased resistance to corrosion and mechanical strength.

Recycling of rhenium from superalloys is an emerging market, with very little recycling actually being carried out currently using scrap super alloy or other alloys, or usually discarded production material.

Concerns and fluctuations in the mined supply of Rhenium are the main driving force behind its recycling. This is due to the fact that mining for Rhenium *per se* is not economically viable; it is actually a by-product of Copper and Molybdenum mining. If the price of either of these metals falls to an uneconomic level, the mine is closed. The U.S. Geological Survey Mineral Commodity Summaries in January 2008 identified the World reserves of this metal to be around 10 million kilograms.

It is known that the current recycling methods employed are quite long (at 6 – 9 months). The properties that the alloy is designed to offer, i.e. high strength, toughness and extraordinary wear resistance, make it a very difficult substance to work with. The preparation of super alloys for Rhenium recycling involves processes that specifically grind these materials. The actual decomposition in turn is carried out by wet chemistry involving heat treatment in mineral acids. This is followed by solvent extraction combined with sulphide precipitation and electro-deposition. Current costs for the process are in the region of $3000 per kg Rhenium recovered, with yields of around 70%. To be commercially attractive, an innovation to recycle rhenium requires added value by re-

ducing the time constraints, reducing costs, increasing yields or a combination of the previous ones.

The present invention includes the manufacturing process of a polymeric material able to trap rhenium in order to obtain highly purified extracts of this metal in a short period of time.

Summary of the Invention

The invention provides a process for forming a porous polymer template material for use in selectively recovering a metal from a solution of the metal ions, comprising polymerising a monomer admixed with a compound of the metal to be recovered, and then treating the polymer to remove the metal compound therefrom.

Preferably, the template material is formed by cross-linking a monomer in the presence of a porogen and said metal compound.

The invention also provides a method of selectively recovering a metal from a solution containing the metal ions, comprising contacting a polymer template material formed by a process according to the invention with the solution containing the metal ions, and recovering the metal from the polymer. The selectivity of the polymer for a specific metal enables an aqueous solution of mixed metal ions, in which the metal of interest may be a minor constituent, to be treated economically.

The invention further provides a polymeric material adapted to capture from a solution containing ions of plural metals a specific one of the metals

Detailed Description of the Invention

The general manufacturing process of the polymer used in the recycling of solutions with an important rhenium content involves the creation of a carbon lattice using a monomer, a cross-linker, initiator and a porogen and the use of a rhenium compound to create a template that is imprinted into this synthetic carbon polymeric material. Following the key-lock principle the rhenium compound found in a concentrated solution of this metal will be trapped selectively and the rest of the solution will be eluted unaffected.

The general process of manufacturing involves the production of the template using a rhenium salt, namely ammonium perrhenate, with a rhenium

concentration ranging between 10-250mg/mL to control the trapping capacity of the polymer. These amounts can be increased to obtain higher yields.

The polymer is manufactured using the following proportions: 5-9% template (such as a rhenium salt), 2-6% monomer (such as vinylpyridine), 42-54% porogen (such as chloroform) and 35-45% of crosslinker (such as Ethyleneglycoldimethacrylate). To finalise the reaction mixture, 90-150mg of initiator (such as 1,1'-azobis(cyclohexanecarbonitrile)) is added to the container.

Once all the chemicals have been added to the reaction container the mixture is vortexed for a period of time not less than 2 minutes. After the complete mixture has been homogenised a flow of nitrogen is pumped into the solution to eliminate all traces of oxygen that might be present for no less than 10 minutes. Once the solution has been purged with Nitrogen, the container is then sealed and then placed in an oven for not less than 48hours, at a temperature of 70°C to allow the solution to polymerise. As the pressure within the container is likely to increase, the material used for the container needs to be able to withstand high pressures.

After the polymerisation is completed the solid polymer is removed from the glass vial and crushed into smaller particles mechanically with aids of mortar and pestle or a ball mill until the particle size is homogenous and the material reaches a sand-type texture.

Once the material has been produced is placed in a column or in a container as the template has to be removed to make it functional and ready to trap rhenium. The template is dislodged by adding to the column or to the container where the material is kept, a 8M solution of hydrochloric acid (pH=-0.8) and left for 20-30 min until all the template has been removed. The final conditioning consists of a washing process of the polymer until the pH of the eluents reach values close to 6-7. A new addition of a solution containing rhenium at pHs close to neutrality will result in rhenium being trapped.

The material can be re-used without loss of the trapping properties or damage to its structure for at least 5 cycles (number tested) but it is believed the durability goes beyond this number of cycles.

Using X-ray Fluorescence (XRF) the molecular imprinted polymer (MIP) could be analysed to determine the percentage of rhenium present within the solid MIP when samples of rhenium solution were eluted through, determining how much rhenium has been trapped by the polymer. Also Fourier transform infrared spectroscopy (FTIR) was also used to determine whether or not rhenium is trapped in the MIP at a wavenumber of 900 cm-1.

It has also been proven that the MIP traps rhenium in a selective way. A solution containing seven different metals present in a typical alloy is proven to retain only rhenium when processed and eluted through the MIP when analysed using XRF.

CLAIMS

1. A process of forming a porous polymer template material for use in selectively recovering a metal from a solution of the metal ions, comprising polymerising a monomer admixed with a compound of the metal to be recovered, and then treating the polymer to remove the metal compound therefrom.

2. A process according to Claim 1, wherein the template material is formed by cross-linking a monomer in the presence of a porogen and said metal compound.

3. A process according to Claim 2, wherein the metal compound is a salt.

4. A process according to any preceding claim, comprising comminuting the polymer after formation.

5. A process according to Claim 2 or 3, wherein the monomer is vinylpyridine.

6. A process according to Claim 5, wherein the porogen is chloroform.

7. A process according to any preceding claim, wherein the polymer is treated with acid to remove the metal compound.

8. A process according to Claim 7, wherein the acid is concentrated hydrochloric acid.

9. A process according to any preceding claim, wherein the metal is rhenium.

10. A process according to Claim 9, wherein the metal compound is ammonium perrhenate.

11. A process of forming a porous polymer template material for use in selectively recovering a metal from a solution of the metal ions, substantially as described herein.

12. A method of selectively recovering a metal from a solution containing the metal ions, comprising contacting a polymer template material formed by a process according to any preceding claim with the solution containing the metal ions, and recovering the metal from the polymer.

13. A method according to Claim 12, wherein the recovering step comprises treatment of the polymer template material with acid.

14. A method according to Claim 13, wherein the acid is concentrated hydrochloric acid.

15. A method of selectively recovering a metal from a solution containing the metal ions, substantially as described herein.

Application No: GB1309308.3 **Examiner:** Dr Kerri Stenning

Claims searched: 1-15 **Date of search:** 12 November 2014

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1, 2, 5-8, 12-14	CN103193928 A (HUAIHAI INST TECHNOLOGY) See English language EPODOC and WPI abstracts.
X	1-5, 7, 8, 12-14	WO2005/063382 A1 (COUNCIL SCIENT IND RES) See page 6 lines 17-20 and examples 1-3 pages 7 and 8.
X	1-3, 5, 7, 12-14	KR100089621 A (UNIV SUNGKYUNKWAN FOUND) See English language EPODOC and WPI abstracts and embodiment 1.
X	1-3, 5, 7, 8	WO2013/063772 A1 (EMPIRE TECHNOLOGY) See paragraph [0040] and example 1 (paragraphs [0057]-[0062]).
X	1, 4, 7, 12-14	CN101864033 A (UNIV JINAN) See English language EPODOC and WPI abstracts and specific embodiments.

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^{X} :

Worldwide search of patent documents classified in the following areas of the IPC

B01D; B01J; C01G; C08J

The following online and other databases have been used in the preparation of this search report

EPODOC, WPI, TXTE, CAS-ONLINE

International Classification:

Subclass	Subgroup	Valid From
C08J	0009/26	01/01/2006