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(54) **Method of preparing rhenium - nickel alloys**

Verfahren zum Herstellen von Rhenium-Nickellegierungen

Procédé de préparation de rhénium - alliages de nickel

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Description

[0001] The subject of this invention is a method for producing homogeneous rhenium - nickel alloys by electrodeposition from aqueous solutions. Rhenium, being a high-melting metal, with a number of unique properties, is gaining on significance as a high quality engineering material. Properties of rhenium promote its application in many areas of technology, such as aviation, space engineering, nuclear engineering, electrical engineering, biomedicine. The application of rhenium as a component of superalloys used, for instance, in the manufacture of jet engine turbine blades, is quickly expanding. Addition of 3 to 6% Re to nickel superalloys enables engine operation at higher temperatures, at higher speed, improving thereby both engine performance and fuel economy. The two currently applied methods of producing metallic rhenium include powder metallurgy (PM) and chemical vapour deposition (CVD). These processes are expensive, complex and energy-consuming. Electrodeposition of rhenium and its alloys, carried out at low temperatures and in nontoxic aqueous solutions, requiring low energy input, may be an alternative to methods applied hitherto. The dense, metallic and uniform cathodic deposits constitute an excellent material for preliminary alloys for creating rhenium-containing special alloys or superalloys.

[0002] A method of forming high temperature resistant rhenium alloy coating films described in patent specification US 7368048 consists in the use of an electrolyte that contains ions of rhenate(VII), alloy metal selected from the group consisting of Ni, Co, Fe and Cr(III), Li and Na, and an organic acid selected from the group consisting of carboxylic acids or aminocarboxylic acids (e.g. citric acid), acting as a complexing agent. This method enables obtaining 10 to 30 μm thick plated films of appropriate quality at a current density of 10 A/dm².

[0003] Patent specification US 3668083 presents a method of electrodeposition of rhenium and its alloys in the form of low-stressed coating films from rhenium bath containing additionally one or more chemical compounds selected from the group consisting of the following salts: magnesium sulphate, magnesium sulphamate, aluminium sulphate and aluminium sulphamate.

[0004] In these processes of obtaining rhenium and its alloys, the agents that provided formation of good quality coating films were additives to the electrolyte in the form of conducting salts, complexing compounds, salts that stabilized processes in the near-electrode zones, or sulphamate ions rendering formation of fine-crystalline deposits of high plasticity and low stress. These processes relate to the forming of thin coatings, rather than to bulk production of solid rhenium alloys.

[0005] The method of preparing electrolytic rhenium - nickel alloys according to this invention consists in the use of a sulphate nickel electrolyte, comprising nickel(II) sulphate, sodium sulphate and boric acid, supplemented by ammonium rhenate(VII) added in an amount of 2 to 100 g/dm³. The cathodic process of depositing the rhenium-nickel alloy proceeds on a centrally arranged cathode. Insoluble anodes are placed on both sides of the cathode. The process is conducted under conditions of stabilizing pH in the near-cathode zone. The method of preparing rhenium-nickel alloys according to the invention consists in electrodepositing them at temperatures of from 10 to 80°C and at current density ≤ 5 A/dm² and pH of the electrolytic bath of from 1 to 8. Under these conditions the obtained rhenium - nickel alloy deposit has a dense, metallic, smooth, uniform structure, and it is produced at a high current efficiency of $\geq 95\%$ and low specific power consumption of within 2.0 to 2.5 kWh per kg of alloy. The cathodic alloy deposits obtained after 48 hours of the electrodeposition process have a thickness > 1.5 mm and the following content of the main components:

Re - ca. 20 to 80 wt% (ca. 7 to 56 atomic %),

Ni - ca. 20 to 80 wt% (ca. 44 to 93 atomic %).

[0006] The advantage of the invention presented is that a dense and uniform deposit of rhenium-nickel alloy is obtained in the form of a solid solution containing up to 80 wt% rhenium. The latter can be used for the production of special alloys. The method according to the invention is illustrated in the examples below.

Example I

[0007] An electrolytic tank is filled with nickel - rhenium electrolytic bath containing 11.5 g/dm³ rhenium in the form of ammonium rhenate(VII), 40.0 g/dm³ nickel in the form of nickel(II) sulphate, 10.0 g/dm³ boric acid and 80.0 g/dm³ sodium sulphate. The process of rhenium - nickel alloy electrodeposition is conducted without electrolyte flow, making up for evaporation losses and for rhenium and nickel ions consumption caused by deposition of the alloy on the cathode, at the temperature of 55°C, at cathodic current density of 1.2 A/dm² and pH of the electrolytic bath of from 1.8 to 4.1. After conducting the process for 48 hours the rhenium - nickel alloy deposit obtained on a copper cathode had a thickness of ca. 1.5 mm; it was dense, metallic, lustrous; it adhered tightly to the core, contained 47.9 wt% rhenium (22.5 atomic %) and 51.9 wt% nickel (77.5 atomic %). The current efficiency of depositing the alloy of the above composition was 99.0%, with specific power consumption amounting to 2.15 kWh per kg of alloy.

Example II

[0008] The process of rhenium - nickel alloy electrodeposition was conducted in a flow electrolyzer, wherein the electrolyte was fed to the bottom of the electrolyzer and was carried away through a weir in the top part of the electrolyzer. The flow of electrolyte was laminar, parallel to the surfaces of the cathode and of the

anodes, stabilizing thereby pH in the cathode area and carrying excess hydrogen ions away from the electrolyzer. The nickel - rhenium electrolyte used contained 13.6 g/dm³ rhenium in the form of ammonium rhenate(VII), 47.8 g/dm³ nickel in the form of nickel(II) sulphate, 10.0 g/dm³ boric acid and 80.0 g/dm³ sodium sulphate. The process was conducted at the temperature of 55°C, at cathodic current density of 1.5 A/dm² and pH of the electrolyte of from 2.4 to 3.6. Linear flow velocity of the electrolyte was 3.0 cm/min, and the volumetric charge density was 3.0 Ah/dm³. After 48 hours of the process the obtained cathodic rhenium - nickel alloy deposit was lustrous, metallic, fine-crystalline, with no cracks or dendrites; its thickness was ca. 1.5 mm; it contained 46.1 wt% rhenium (21.4 atomic %) and 53.5 wt% nickel (78.6 atomic %). The current efficiency of depositing this alloy was 99.9%, with specific power consumption amounting to 2.13 kWh per kg of alloy.

Claims

1. Method for producing homogeneous rhenium - nickel alloys by electrodeposition from aqueous solutions, **characterized in that** to a sulphate nickel electrolytic bath for cathodic nickel production rhenium is introduced in the form of rhenate(VII) ions, preferably in the form of ammonium rhenate(VII), in an amount of from 2 to 100 g/dm³, and at a temperature of from 10 to 80°C, preferably at a temperature close to 55°C, the process of rhenium - nickel alloy electrodeposition is conducted on a cathode arranged centrally in an electrolyzer, with two insoluble anodes placed on both sides of the cathode, said cathodes preferably made of titanium and coated with metal oxides, wherein the cathodic current density is set to ≤ 5 A/dm², with pH of the bath ranging from 1 to 8, and wherein a laminar flow of the electrolyte is effected at a linear velocity of from 1 to 5 cm/min for a volumetric charge density ranging from 1 to 5 Ah/dm³.

Patentansprüche

1. Die Gewinnungsart homogener Rhenium-Nickel-Legierungen durch Elektroabscheidung aus Wasserlösungen, die sich dadurch charakterisiert, dass in ein Nickelsulfat-Elektrolytenbad, das zur Herstellung von Nickelkathoden verwendet wird, 2 bis 100 g/dm³ Rhenium in Form von Rhenat(VII)-Ionen am besten als Ammonium(VII)-Rhenat eingeführt werden und bei einer Temperatur von 10 bis 80°C, am besten bei ca. 55°C an einer im Elektrolyseur zentral angebrachten Kathode an deren beiden Seiten unlösliche Anoden, um besten Titananoden mit Metalloxiden beschichtet, anzubringen sind die Elektroabscheidung einer Rhenium-Nickel-Legierung erfolgt.

Dabei sind die Kathodenstromdichte von ≤ 5 A/dm² und der pH-Wert des Elektrolyten 1 bis 8 anzupassen. Der laminare Elektrolyten-Durchfluss hat mit einer Längsgeschwindigkeit von 1 bis 5 cm/min für die elektrische Ladungsschicht von 1 bis 5 Ah/dm³ zu erfolgen.

Revendications

1. Procédé d'obtention des alliages homogènes de rhénium-nickel en voie d'électroextraction des solutions aqueuses, **caractérisé en ce qu'**au bain électrolytique de sulfate de nickel utilisé pour la fabrication du nickel cathodique on introduit du rhénium sous forme des ions de rhénium(VII) avantageusement en tant que rhénate(VII) d'ammonium en quantité de 2 à 100 g/dm³ et à température comprise entre 10 et 80°C, avantageusement à température proche de 55°C, on réalise le procédé d'électroextraction de l'alliage de rhénium-nickel sur une cathode placée au centre de la cuve électrolytique, de deux côtés de la cathode il y a des anodes insolubles, avantageusement en titane, revêtues d'oxydes métalliques, la densité cathodique de courant étant fixée à ≤ 5 A/dm², le pH du bain étant de 1 à 8, étant précisé qu'on assure un flux laminaire de l'électrolyte à vitesse linéaire de 1 à 5 cm/min pour la capacité volumique de la charge électrique de 1 à 5 Ah/dm³.

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

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- US 3668083 A [0003]