UDC 669.054:[27+28]

G.A. Kolobov (1), professor, c.t.s.
K.A. Pecheritsa (2), director
A.V. Karpenko (1), assistant
Yu.V. Mosejko (1), associate professor, c.p.s.
V.N. Ochinsky (1), senior teacher

AFFINAGE OF TUNGSTEN AND MOLYBDENUM

Zaporozhe state engineering academy, Ukraine
LTD «Trade», Zaporozhe, Ukraine

There are considered technologies of affinage of tungsten and molybdenum: electrolytic, method of chemical transport reactions (thermal dissociation of chlorides), refining melting (including. vacuum arc, cathode-ray, area and plasma-induction) and complex methods. The choice of method of affinage is determined by the degree of cleanness and chemical composition of initial metal.

Keywords: tungsten, molybdenum, electrolysis, thermal dissociation, burning, refining melting, vacuum technologies, complex methods

Introduction. Tungsten and molybdenum is included in the sub-group of refractory rare metals (temperature of melting 3395 ± 15 °C and 2620 ± 10 °C according). Basic industrial method of receipt of tungsten and molybdenum is reduction of them trioxides hydrogen to metallic powder. The compact billets of these metals get by the methods of powder-like metallurgy or melting. For some application areas a cleanness of tungsten and molybdenum, got on the generally accepted technology, is insufficient. For the receipt of high-clean tungsten and molybdenum use different chemical, electrochemical and physical and chemical methods, but the process of affinage complete, as a rule, physical methods, in basis of which such processes, as evaporation and condensation, diffusion and crystallization, are the basis of, electro migration et al underlie [1,2].

The different aspects of physical methods of affinage of rare metals are considered in works of the «Kharkov phyzical-technics institute» [3-5]. For the deep cleaning of metals used such methods of affinage, as distillation, high-vacuum annealing, cathode-ray melting, zone recrystallization and electromigration. The receipt of metals of high-purity is closely related to vacuum conditions which the final cleaning is at. In most cases at an affinage chemically active refractory rare metals limiting a cleaning process there are gas and gaseous additions of introduction: nitrogen, hydrogen, oxygen and carbon. Cleaning from these additions takes place due to the selection of them as gas at heating of the refined metal in a vacuum, in this connection a large value is acquired the questions of improvement of a vacuum environment. In work [3] influence of vacuum conditions: degrees of vacuum (pressures of remaining gases), accumulating in a vacuum system, cleanness's of vacuum (composition of remaining gases) on content of additions in rare metals, including. tungsten and molybdenum is experimentally studied. The increase of cleanness of vacuum and decline of remaining pressure due to application of histrionic and sublimation facilities of exhaust assist a deeper affinage from the additions of introduction and increase of metal cleanness. The row of metals (rhenium, ruthenium and osmium) was got, on the level

of cleanness of not having analogues in world practice, and the level of cleanness of many other rare metals, including, tungsten and molybdenum, corresponds to the best foreign achievements [4,5].

Electrolytic affinage. As well as other refractory rare metals, a technical molybdenum and tungsten can be cleared by the method of electrolytic affinage [6]. In a patent № 918167 (Great Britain) for the electro-affinage of molybdenum it is suggested to use an electrolyte, consisting of 30-80 % $CaCl_2$ and 10-40 % MoO_3, with the temperature of melting 700 °C. Experiments executed at a temperature 1050-1200 °C, at the anodic closeness of current to 4.0 A/sm^2, at its cathode closeness – 1.5-11.0 A/sm^2 with the use of cathode from titan, molybdenum, tungsten or iron. A metal was got with cleanness 99.80-99.99 % and it is ascertain that presence in the electrolyte of salts of alkaline metals assists contamination of cathode product.

In the same patent the electro-affinage of technical tungsten it is suggested to execute in an electrolyte, containing 30-80 % $CaCl_2$ and 10-35 % WO_3. Such electrolyte melts at a temperature 700 °C, but steady to the temperature 1400 °C. As cathode material used titan, tungsten, molybdenum or iron as at the affinage of molybdenum. A process was carry out at the cathode closeness of current 1.5-11.0 A/sm^2 and anodic - to 4.0 A/sm^2. Brilliant large crystals were got with cleanness 99.80-99.99 % tungsten. Specified, that a presence in the electrolyte of salts of alkaline metals fosters to contamination of cathode product.

In work [7] for the electro-affinage of aluminothermy molybdenum fusion of KCl is recommended - K_3MoCl_6, containing an about 7.5 % molybdenum. Researches executed in the environment of argon at a temperature 900 °C, to the cathode closeness of current 0.75-0.88 A/sm^2 with a cathode from stainless steel. An output of clean metal is 85 %. In the same work, as most perspective for the affinage of tungsten, the electrolytes of two compositions are examined: 1) 60 % KCl, 30 % NaF, 10 % WCl_6 and 2) 50 % $Na_4P_2O_7$, 40 % $NaCl$, 10 % WO_3. The regime of electrolysis is indicated for the first electrolyte: cathode closeness of current 0.6 A/sm^2, anodic closeness of current – 0.1 A/sm^2, temperature of process – 700-800 °C.

In works [8,9] the method of receipt of clean macrocrystalline tungsten by the electrolytic affinage of its wastes (piece of beads, sticks and other) is considered in chloride-fluoride fusion (60 % $NaCl$, 15 % NaF, 25 % WO_3) at maintenance of inert atmosphere in working space of electrolyzer. Tungsten was besieged on a molybdenum cathode as separate needle-shaped crystals and joints. The technological parameters of process: cathode closeness of current – 0.4-1.0 A/sm^2, anodic – 0.1 A/sm^2, temperature - 800 ± 20 °C. In the process of electrolysis the concentration of tungsten in an electrolyte remains by permanent to the degree making of soluble anode 50-55 %. In future an electrolyte begins to be impoverished on tungsten and at the 70-75 % making of anode a process must finish or loading fresh anodic material. The got cathode deposits of tungsten wash from an electrolyte in 3 % solution of alkali, after wash in 1 % solution of hydrochloric acid and distilled water, and then expose to drying at a temperature 60-80 °C. Basis mass of powder-like cathode metal is presented by factions: - 1. +0,4 mm (~35 %) and are a 0.4 mm (~55 %). On most additions cathode tungsten powders approximately on an order cleaner refined metal. It is marked that

is provided good cleaning of tungsten from a carbon and silicon, worse - from molybdenum. Such powders are suitable for meltback in a bar or converting into compact billets by the method of isostatical hot-pressed.

In work [10] for the receipt of fine-crystalline powder of tungsten an electrolyte is offered, containing %: 38-42 *KF*; 38-42 *KCl*; WCl_6 - other. Tungsten powder with content of basic component 99.8 % was got at the cathode closeness of current 0.8 A/sm^2 and temperature of process 750 °C.

Affinage by a method of chemical transport reactions (*CTR*). Method of iodide affinage, as variety of method of CTR, for cleaning of tungsten and molybdenum is inapplicable, as both metals do not co-operate with iodine. However for the receipt of clean tungsten and molybdenum other variety of method of CTR is thermal dissociation of their higher chlorides (WCl_6 and $MoCl_5$) on a burning hot filament can be used. As it applies to molybdenum this process is described by a next reaction:

$$\underset{\text{(tech.)}}{2Mo_{(h)}} + 5Cl_{2(g)} \overset{T_1}{\Rightarrow} 2MoCl_{5(g)} \overset{T_2}{\Rightarrow} \underset{\text{(clean)}}{2Mo_{(h)}} + 5Cl_{2(h)} \ , \qquad (1)$$

where $T_1 > T_2$.

Speed of besieging of molybdenum on a filament has a maximal value at the temperature of initial molybdenum 300-400 °C, when co-operating of molybdenum with chlorine is most active. At the further increase of temperature there is the secondary co-operating of pentachloride molybdenum ($MoCl_5$) with initial molybdenum with formation of hard trichloride of molybdenum ($MoCl_3$) on a reaction:

$$3MoCl_{5(газ)} + 2Mo_{(тв)} \Leftrightarrow 5MoCl_{3(тв)} \ . \qquad (2)$$

Hard $MoCl_3$, put aside on the surfaces of the refined (initial) molybdenum, hinders to its contact with chlorine: a reaction (1) damps and deposit of metal on a filament at a temperature 500-600 °C ends.

In respect of influence of temperature of filament, then with its increase there is an increase of speed of molybdenum deposit. It is explained, obviously, by the increase of value of constant of equilibrium for reaction of thermal dissociation as far as the increase of temperature. The optimal regime of besieging of molybdenum from his higher chloride answers the temperature of filament 1300-1400 °C, to the temperature of initial molybdenum 300-400 °C and pressure of $MoCl_5$, equal 40 Pa. The got molybdenum is characterized by small content of additions (oxygen, nitrogen, hydrogen et al) and high plasticity as compared to an initial metal [1].

Clean tungsten can be got at reduction of its hexafluoride (WF_6) by hydrogen on the heated surface. For the receipt of high-clean tungsten by the method of hydrogen reduction of its hexafluoride the special apparatus with the different variants of reactionary chambers and technological rigging is worked out. For every type of the got products the technological parameters of process of besieging of tungsten are optimized [11].

Annealing and refining melting. On the basis of analysis of researches, sacred to the problem of affinage of refractory rare metals from the additions of introduction, in work [12] for cleaning of molybdenum (and tungsten) the method of a vac-

uum high temperature diffusive annealing is offered and influence of technological parameters of process on quality of cleaning is investigated.

At the use of new technologies of melting (vacuum arc, cathode-ray and zone) in the process of draft metal remelt of there is not only his melting but also there is a refining effect. First of all it touches vacuum types of melting which provide the good degassing of metals. Calculations show that, unlike titan, zirconium, vanadium and, partly, niobium and tantalum, at a vacuum melting of tungsten and molybdenum a cleaning degree is arrived at from oxygen in 4900 and 7350 times accordingly. Really, as shown experimentally, decline of concentration of oxygen in a molybdenum from 0.32 to 0.03 % arrived at for 3-5 minutes. Speed and degree of moving away of oxygen at melting in a vacuum are increase, if in a tungsten and molybdenum there is a carbon (because of education *CO*). Except for gas additions and carbon, at vacuum arc (remaining pressure is 10^{-1}-10^{-3} Pa) and cathode-ray (remaining pressure is 10^{-3}-10^{-5} Pa) melting of refractory rare metals concentration in them comparatively well volatile metals: alkaline, alkaline-earth et al (magnesium, zinc, lead, copper, tin, nickel, iron) goes down. Thus, than anymore difference in volatility of the refined metal and metals-additions, contained in it, the more effective cleaning flows [13].

The cathode-ray melting of tungsten and molybdenum with a consumed electrode is a very effective mean for the receipt of compact plastic billets (bars and sticks) with minimum content of gas additions. So, for example, cathode-ray melting of 99,8 % molybdenum at a temperature 2700 °C and remaining pressure 0,0013 Pa with self-control of liquid metal during 15 mines a molybdenum was got by a cleanness higher 99,99 %. As a result of melting content of oxygen, nitrogen, carbon, silicon, phosphorus, iron, copper and cobalt goes down considerably. Oxygen retires not only as his oxide (With) but also, possibly, as *MoO*, nitrogen vanishes in a molecular form. Silicon, phosphorus and metallic additions, is sublimated during melting, because pressure of their steams higher than pressure of steam of molybdenum in 103-108 times [1].

Method of receipt of tungsten of high-purity on a patent [14] can be applied at the production of bars of high-clean tungsten, and also flats from a high-clean tungsten for the use in microelectronics, quantum electronics, solar radiation engineering and electrical engineering. Technology foresees a vacuum affinage by the first remelt the cathode-ray melting (CRM) and by second remelt an electroarc vacuum melting (EVM) with consolidation of fusion in crystallizers in bars. By source material are metal ceramics sticks, got from the powder-like unalloyed tungsten. EVM carry out at intensive interfusion of fusion by electromagnetic field of solenoid with forming of fine-grained structure of bars of tungsten. Correlation by the diameters of crystallizers for the first and second remelts $d_1/d_2 = 0.57$ makes.

Method of receipt of molybdenum of high-purity on a patent [15] is analogical to the method for receipt of high-clean tungsten [14]. A difference consists only that CRM of molybdenum carry out at a speed of 0.5-0.6 kg/of mines, and correlation by the diameters of crystallizers makes $d_1/d_2 = 0.6$.

A method of the cathode-ray melting with an intermediate capacity (CRMC) is one of refining remelts. In work [16] the bars of molybdenum got the method of

CRMC with the use of the peripheral heating of metal in crystallizer is investigated. The degree of affinage of molybdenum from additions in dependence on the parameters of melting and mechanical properties of the smelted bars is certain.

In the method of receipt of molybdenum of high-purity on a patent [17] a vacuum affinage is executed by two successive cathode-ray remelts. The first remelt of initial metalceramic billet in a bar is carry out with small speed, and the second is carried out with maximally possible high-rate for forming of fine-grained structure of bar. Correlation by the diameters of crystallizers for the first and second remelts makes $d_1/d_2 = 0.5$. Crystallization of fusion is carried out in vertically crystallizers of round or cuboid section with the receipt of cylindrical or cuboid bars or in horizontal round or cuboid crystallizers with the receipt of cylindrical or rectangular flat bars. The got bars of high-clean molybdenum can be rolled in a sheet, foil, wire or from them targets can be made for magnetron dispersion.

Presently a vacuum cathode-ray melting is widely used for the remelt of molybdenum scrap with the receipt of clean foods (bars and ready-to-cook foods). So, in a patent № 480332 (Japan) there is offered the method of processing of wastes of molybdenum and tungsten in a clean bar. Example: there is melted molybdenum scrap in a cathode-ray furnace (remaining pressure is 0.13-0.013 Pa, power is 1200 kW, the productivity is 50 kg/hour) with the receipt of bar sizes 1570×470×150 mm. The content of additions made in a charge and bar, % 10^{-4}: Al - 10 and 5, Fe - 50 and 20, Ti - 25000 and 10, O - 111 and 4, N - 10 and 1, C - 175 and 25, S 1, H 1.

By the method of cathode-ray remelt of molybdenum scrap a high-clean molybdenum wire was got for the pendants of tungsten filament in incandescent lamps. The effect of affinage was looked after as a result of double remelt of charge in a bar: content (million $^{-1}$) of oxygen went down from 600 to 20, carbon - from 260 to 50. Wire from a bar a diameter a 105 mm was got by implementation of next successive operations: cutting of bar, extrusions of billets, forgings of billets in sticks and broach of sticks in a wire by diameter 0.12 mm. With the purpose of cleaning from greasing and increase of durability a wire was exposed to annealing in the atmosphere of moist hydrogen [18].

Crestalphisics affinage (zone melting). The most clean molybdenum and tungsten is got by the zone melting. So, relation of electric resistance R(300 K) / R(4.2 K) for a molybdenum and tungsten after the zone melting in a vacuum ~ 10^{-4} Pa are 60000 and 70000 accordingly. Interestingly, that realization of the zone melting in the analogical conditions of such metals however vanadium, niobium and zirconium, allows to get a metal with the relation of electric resistance more than 500 [3].

The affinage of molybdenum and tungsten at the zone melting takes place not only due to evaporation of additions, but also due to their zone redistribution. Most metallic additions are had coefficient of distribution in a molybdenum less, therefore cleaning from them at the zone melting of molybdenum is effective. Most the difficult deleted metallic additions are served: for molybdenum is tungsten, chrome, silicon and other refractory elements, for tungsten is a molybdenum, rhenium and tantalum.

By basic non-metal additions, limiting the cleanness of tungsten and molybdenum, there are a carbon and, in less degree, oxygen. With the increase of number of

passage-ways of zone the cleanness of metals rises, the level of content of metallic, gas additions and carbon goes down. Sometimes for the decline of carbon content the zone melting of molybdenum and tungsten is executed in the rarefied environments of oxygen and hydrogen.

The method of the floating-zone refining with the use of the cathode-ray and plasma arc heating allows to get the single-crystals of refractory metals of high-purity. On the example of receipt of single-crystals of tungsten and molybdenum in-process [19] it is shown that cleaning efficiency is observed already as a result of two passage-ways of area, and as a result of the cathode-ray area melting at imposition of electric-field tension 0.25 V/sm for four passage-ways of area a tungsten was got with relative specific electric resistance to 60000.

The affinage of quasi-eutectic alloys of refractory metals (molybdenum, niobium, and tantalum) with high content of carbidic phase has the specifics, both at the floating-zone refining and in a post-crystallization period [20]. In the process of post-crystallization treatment the considerable increase of cleanness of matrix constituent of alloys is accompanied by the redistribution of phases. So, in the system *Mo-ZrC* caught-on behind after crystallization which crisped carbides of Mo2C at annealing practically fully taken in by the carbides of zirconium, effectively clearing a molybdenum matrix.

Paton institute of the electric welding of NASU for growing of single-crystals of tungsten the plasma-induction melting is offered [21,22].

Refining ability of the plasma melting is determined, unlike the traditional zone melting, by the drop mechanism of transfer of metal in bath. Thus the process of affinage flows at all stages: at burn-off of initial stick, in a drop and bath. It is marked that, unlike the cathode-ray zone melting, the plasma-induction melting allows more effectively to delete a carbon and oxygen from a tungsten, because at such combined heating and surplus pressure in the furnace chamber the sources of carbon butters related with hit of oil steams in the volume of furnace are removed, and the content of carbon in a metal oxidizes and retires.

The further increase of cleanness of tungsten and molybdenum can be attained by the maximally complete moving away from the initial material of additions, hard-to-remove zone melting, and realizations of process in «withoutoil» vacuum.

Complex methods of affinage. The most clean molybdenum and tungsten were got by application of complex methods of affinage. So, for the decline of content of additions in a molybdenum, which badly retire in the process of the zone melting, used the chemical method of affinage, including chlorinating of initial powder of molybdenum with subsequent distillation of $MoCl_5$ [2]. A similar chart allowed considerably to reduce content in the molybdenum of tungsten and row of other additions.

In other example for the receipt of high-clean single-crystals of molybdenum and tungsten the complex chart of affinage, which plugged in itself pre-cleaning of trioxides molybdenum (MoO_3) and tungsten (WO_3) with subsequent their hydrogen reduction and floating-zone refining of the cleared metal in a vacuum, was used. For cleaning MoO_3 was applied method of zone sublimation, that allowed considerably to reduce content in MoO_3 of tungsten, niobium, iron, silicon and other additions. Cleaning of WO_3 was carried out by heat treatment in oxygen, here from WO_3 de-

leted as oxides a molybdenum, carbon and other additions. At the hydrogen reduction of trioxides molybdenum and tungsten there was cleaning of them from a carbon, sulphur and oxygen [2].

Complex method of receipt of high-clean tungsten, intended for thin-film metallization by magnetron dispersion of targets [23], foresees cleaning of paratungstate of ammonium (PTA) in the beginning by the sulfide of ammonium from the additions of molybdenum, and then by an ionic exchange on the anionite of AM-n. By thermal decomposition PTA at a temperature 600-800 °C got a tungsten anhydride which was cleared by zone sublimation at a temperature 900-950 °C in the direct flowing of oxygen. By hydrogen reduction of WO_3 at a temperature 700-750 °C got metallic powder of tungsten and pressed it in stick. Stick was exposed to the cathode-ray zone melting with the receipt of single-crystal flat bar which in the vacuum of melt from every side to all depth of no less than two times. Thus bar before the floating-zone refining was processed by chlorine at speed of serve 100 ml/mines and to the temperature 300 °C during one hour.

The similar method of receipt of high-clean molybdenum, intended for thin-film metallization by magnetron dispersion of targets, includes the enumerated below chemical and metallurgical operations [24-26]. Cleaning of patamolybdate ammonium from additions was executed by the method of ionic exchange in neutral and alkalescent environments on the hydrated oxide of tin and on the weakly main anionite of AH-106. By thermal decomposition of PTA at a temperature 600-800 °C got a molybdenum anhydride which was cleared by zone sublimation at a temperature 750-800 °C in the flowing of oxygen and then restored hydrogen at a temperature 700-750 °C to metallic powder of molybdenum. Powder was pressed in stick which was exposed to the cathode-ray zone melting with the receipt of single-crystal flat bar (of target). In flat crystallizer bar melts from every side to all depth of no less than two times. Thus before the floating-zone refining stick was processed by a chlorine at speed of serve 100 ml/mines and to the temperature 300 °C during one hour.

Complex technology, worked out in «Bhabha Atomic Research Centre» (India) [27], it was applied at the receipt of powder of molybdenum of high-purity from sour solutions, appearing at processing of molybdenum scrap. Technology plugged in itself: adsorption of molybdenum on coal, desorption by its ammonia, besieging from solution of molybdate of ammonium, its calcinations' to MoO_3 and two-phase reduction of MoO_3 by hydrogen. The content of additions in the got powder made, mil^{-1}: $Fe < 100$, Ni, Cr, Al, Mn, $Pb < 20$, $Co < 30$, K, $Mg < 10$, $Sn < 200$, $Cu < 6$.

Conclusion. The choice of one or another method of affinage of tungsten and molybdenum is determined by the degree of cleanness and chemical composition of initial metal. Achievement of the greatest degree of cleanness of tungsten and molybdenum possibly by application of complex methods of affinage with the finish use of physical methods of affinage in the conditions of deep vacuum.

REFERENCES

1. Беляев, А. И. Металлургия чистых металлов и элементарных полупроводников : учебн. пособие [Текст] / А. И. Беляев, Е. А. Жемчужина, Л. А. Фирсанова. – М. : Металлургия, 1969. – 504 с. – Библиогр. : с. 488-499.

2. Тихинский, Г. Ф. Получение сверхчистых редких металлов [Текст] / Г. Ф. Тихинский, Г. П. Ковтун, В. М. Ажажа. – М. : Металлургия, 1986. – 160 с. – Библиогр. : с. 153-161.
3. Вакуум в металлургии особо чистых металлов [Текст] / В. М. Ажажа, П. Н. Вьюгов, С. Д. Лавриненко, Н. Н. Пилипенко // Специальная металлургия : вчера, сегодня, завтра : материалы междунар. науч.-техн. конф. (г. Киев, 8-9 окт. 2002 г.). – Киев : ІВЦ «Видавництво «Політехніка», 2002. – С. 73-78.
4. Ажажа, В. М. Получение и металлофизика особо чистых металлов [Текст] / В. М. Ажажа, Г. П. Ковтун, Г. Ф. Тихинский // Металлофизика и новейшие технологии. – 2000. – Т. 22. - № 2. – С. 21-35.
5. Ажажа, В. М. Редкие металлы высокой чистоты и их свойства [Текст] / В. М. Ажажа, Г. П. Ковтун, П. Н. Вьюгов // Благородные и редкие металлы : сб. материалов 3-й междунар. конф. «БРМ-2000». – Донецк : ДонГТУ, 2000. – С. 333.
6. Сучков, А. Б. Электролитическое рафинирование в расплавленных солях [Текст] / А. Б. Сучков. – М. : Металлургия, 1970. – 256 с. – Библиогр. : с. 244-255.
7. Васько, А. Т. Электрохимия тугоплавких металлов [Текст] / А. Т. Васько, С. К. Ковач. – Киев : Техніка, 1983. – 160 с. – Библиогр. : с. 157-159.
8. Павловский, В. А. Электролитический способ получения катодного кристаллического вольфрама [Текст] / В. А. Павловский, В. А. Резниченко // Технология металлов. – 1999. – № 7. – С. 2-3.
9. Колобов, Г. А. Металлургия редких металлов. Часть 1. Вторичный вольфрам [Текст] : Учебн. пособие / Г. А. Колобов. – Запорожье : ЗГИА, 2004. – 44 с. – Библиогр. : с. 42.
10. А.с. 547482 СССР, МПК С 25 С 3/00. Электролит для электролитического получения мелкокристаллического порошка вольфрама [Текст] / Сучков А. Б., Ковалев Б. Ф, Рабинович Е. М. и др. (СССР). – № 218043502 ; – заявл. 10.10.75 ; опубл. 25.02.77, Бюл. № 7.
11. Колобов, Г. А. Извлечение из вторичного сырья и рафинирование тугоплавких редких металлов [Текст] / Г. А. Колобов, В. В. Павлов, Ю. В. Мосейко // Теория и практика металлургии. – 2014. – № 1-2 (96-97). – С. 109-113.
12. *Дзядыкевич*, *Ю. В.* Исследование процесса очистки молибдена и вольфрама от примесей внедрения [Текст] / Ю. В. Дзядыкевич, Р. М. Горбатюк // Высокочистые вещества. – 1996. – № 1. – С. 57-61.
13. Колобов, Г. А. Рафинирование цветных металлов. Физико-химические и технологические основы [Текст] / Г. А. Колобов, С. И. Давыдов, К. А. Печерица. – Запорожье : Просвіта, 2012. – 160 с. – Библиогр. : с. 155-160. – ISBN 66-935.5:669-034.2/8.
14. Способ производства вольфрама высокой чистоты : пат. 2349658 Россия, МПК С 22 В 34/36 (2006.01), С 22 В 9/20 (2006.01) / В. Г. Глебовский, Е. Д. Штинов, А. И. Пашков, О. С. Кочетов ; патентообладатель В. Г. Глебовский. – № 2007140539/02; заявл. 02.11.2007; опубл. 20.03.2009.
15. Способ производства молибдена высокой чистоты: пат. 2349657 Россия, МПК С 22 В 34/36 (2006.01), С 22 В 9/20 (2006.01) / В. Г. Глебовский, Е. Д. Штинов, А. И. Пашков, О. С. Кочетов ; патентообладатель В. Г. Глебовский. – № 2007140538/02; заявл. 02.11.2007; опубл. 20.03.2009.
16. Мушегян, В. О. Исследование структуры и механических свойств молибдена, полученного способом ЭЛПЕ [Текст] / В. О. Мушегян, Е. Н. Потятыник // Современная электрометаллургия. – 2012. – № 12. – С. 31-33.
17. Способ производства молибдена высокой чистоты Глебовского: пат. 2351669 Россия, МПК С 22 В 34/36 (2006.01), С 22 В 9/20 (2006.01) / заявители В. Г. Глебовский, Е. Д. Штинов, А. И. Пашков, О. С. Кочетов ; патентообладатель В. Г. Глебовский. – № 2007140537/02; заявл. 02.11.2007; опубл. 10.04.2009.
18. *Колобов*, *Г. А.* Металлургия редких металлов. Часть 2. Вторичный молибден [Текст] : учебн. пособие / Г. А. Колобов. – Запорожье : ЗГИА, 2005. – 27 с. – Библиогр. : с. 26.
19. Солопихин, Д. А. Применение зонной перекристаллизации для получения высокочистых тугоплавких металлов [Текст] / Д. А. Солопихин // Вопросы атомной науки и техники. – 2007. – № 4. – С. 204-210.
20. Семененко, В. Е. Особенности зонной перекристаллизации сплавов тугоплавких металлов с высоким содержанием углерода [Текст] / В. Е. Семененко, Н. Н. Пилипенко // Вопросы атомной науки и техники. – 2007. – № 4. – С. 143-148.

21. Рафинирование вольфрама в процессе плазменно-индукционного выращивания монокристаллов [Текст] / В. А. Шаповалов, Ю. В. Латаш, И. В. Шейко и др. // 10-я конф. по химии высокочистых веществ : тезисы докладов. – Н.Новгород, 30 мая-1 июня 1995 г. – Н. Новгород : ИХВВ РАН, 1995. – С. 98.
22. Рафинирование вольфрама при плазменно-индукционном выращивании монокристаллов [Текст] / В. А. Шаповалов, И. В. Шейко, Ю. В. Латаш, В. В. Жолудь // Проблемы специальной электрометаллургии. – 1977. – № 2. – С. 43-48, 85.
23. Способ получения высокочистого вольфрама для распыляемых мишеней: пат. 2434960 Россия, МПК C 22 B 34/36 (2006.01), C 22 B 3/24 (2006.01) / заявители Институт физики твердого тела РАН, В. Г. Глебовский, Н. С. Сидоров, Е. Д. Штинов ; патентообладатель В. Г. Глебовский. – № 2010137604/02; заявл. 10.09.2010; опубл. 27.11.2011.
24. Способ получения высокочистого молибдена для распыляемых мишеней и устройство для его реализации: пат. 2375479 Россия, МПК C 22 B 34/34 (2006.01), C 22 B 3/20 (2006.01) / заявители В. Г. Глебовский, Н. С. Сидоров ; патентообладатель Институт физики твердого тела РАН. – № 2008125866/02; заявл. 26.06.2008; опубл. 10.12.2009.
25. Способ получения высокочистого молибдена для распыляемых мишеней : пат. 2434959 Россия, МПК C 22 B 34/34 (2006.01), C 22 B 3/24 (2006.01) / В. Г. Глебовский, Н. С. Сидоров, Е. Д. Штинов ; патентообладатель Институт физики твердого тела РАН. – № 2010137605/02; заявл. 10.09.2010; опубл. 27.11.2011.
26. Глебовский, В. Г. Исследование процессов получения высокочистого молибдена [Текст] / В. Г. Глебовский, Е. Д. Штинов, Н. С. Сидоров // Перспективные материалы. – 2011. – № 11. –С. 51-53.
27. Bidaye, A. C. Recovery of reactive and refractory metals from their respective scrap. Molibdenum [Text] / A. C. Bidaye, J. G. Sharma // BARC News lett. – 2003. – No 237. – P. 140-142.