**Вісник Тернопільського національного технічного університету**
**https://doi.org/10.33108/visnyk_tntu**
Scientific Journal of the Ternopil National Technical University
*2024, № 3 (115) https://doi.org/10.33108/visnyk_tntu2024.03*
*ISSN 2522-4433. Web:* ***visnyk.tntu.edu.ua***

**UDC 668.045.18**

# HEAT TREATMENT OF MOLYBDENUM AND TUNGSTEN IN POWDER ENVIRONMENTS

**Vasiliy Kovbashyn[1]; Igor Bochar[2]**

*[1]Ternopil Ivan Puluj National Technical University, Ternopil,Ukraine*
*[2]Ternopil Volodymyr Gnatyuk National Pedagogical University, Ternopil, Ukraine*

***Abstract.*** *The recommended ways of improving the technological and physico-mechanical properties of refractory metals (molybdenum and tungsten) after diffusion annealing in several stages are described. In order to significantly increase the technological characteristics and transition to stricter conditions of operation of products made of refractory metals, it is necessary to improve the already existing methods of metal processing and make significant changes in the development of new ones. Different directions of processing of refractory metals have been studied and analyzed, which involve the process of heating and cooling of metals, while their near-surface layers receive certain complex technological processes of redistribution of chemical components. A certain part begins to migrate to the surface of the metal-vacuum distribution, another part moves into the depth, and still another part remains without movements. The behavior of carbon, oxygen and nitrogen penetration elements was studied when molybdenum and tungsten were heated to a temperature of 800 °C and then cooled to room temperature. To evaluate changes in the mechanical properties of molybdenum and tungsten after diffusion annealing, appropriate tests were conducted. In order to study the changes in the technological and physico-mechanical properties of refractory metals after the process of diffusion annealing in an active powder environment, bending and buckling tests were conducted. Conducted studies on the content of oxygen in refractory metals during the second heating showed that its concentration in tungsten decreases by almost two times, and in molybdenum by five times. The technological process of purification refractory metals can be significantly accelerated if molybdenum and tungsten are heated in pulse mode, which involves heating and cooling, as is known, this method of thermal treatment of metals stimulates the processes of transfer of impurities penetrating from the depth of the volume of metals to their surface. The conducted studies established that after the first diffusion annealing, the plasticity coefficient of molybdenum increased by 3–4 times, and that of tungsten by 2–3 times, compared to untreated samples of refractory metals. Based on the analysis of literature data and conducted research, a set of measures aimed at improving the technological and physico-mechanical properties of refractory metals (molybdenum and tungsten) after diffusion annealing in an active powder environment is proposed.*
***Key words*****:** *molybdenum, tungsten, plasticity, heat treatment*.

*https://doi.org/10.33108/visnyk_tntu2024.03.023* *Received 21.07.2024*

## 1. INTRODUCTION

The use of molybdenum (*Mo*) and tungsten (*W*) of technical purity has revealed their high brittleness at normal and low temperatures, and especially during welding or recrystallisation. As a result, their use in high-temperature equipment and technological processes is significantly limited [1]. One of the reasons for this limitation is the presence of harmful impurities along the grain boundaries of these metals.

## 2. EXPERIMENTAL METHODS

When using refractory metals, it is necessary to consider that penetrating impurities are practically insoluble in them and thus compounds containing penetrating elements – in particular, oxides and carbides – are always formed, and they are located mostly along the grain boundaries, significantly reducing the bond between them.

*Corresponding author: Vasiliy Kovbashyn; e-mail: kovbashyn_v@ukr.net* 

The results of the research [2] made it possible to identify the main causes of the destruction of bonds between grains:

- equilibrium segregation of harmful elements such as oxygen, carbon, nitrogen, hydrogen;
- thin films that can cover more than half of the grain surface;
- local internal stresses within the grain boundaries in the process of strengthening the boundary zones by unbalanced segregation;
- dispersive hardening of the grain body to create zones free of various emissions.

An extensive analysis of works [3–7] on the study of the problems of increasing the plasticity of *Mo* (molybdenum) and *W* (tungsten) by annealing them in various chemically active environments, as well as previous studies [2] by the authors of this publication, suggests that low-temperature treatment of refractory metals in a confined space with a rarefied environment (vacuum furnace), as well as by absorbing penetrating elements with a powder medium containing active chemical components, would be promising.

The aim of the investigation is to study the effective methods of diffusion purification of molybdenum and tungsten from harmful impurities not to strengthen the metal structure, but to increase their plasticity.

## 3. RESULTS AND DISCUSSION

For X-ray diffraction studies of the structure of *Mo* (molybdenum) and *W* (tungsten), monochromatic radiation was used on a *DRON* diffractometer. The features of the fracture surface formed during bending of refractory metals were studied by Auger microprofileometry and ion etching. All the experiments were performed on the *LAS* instrumentation. Auger spectrometry ensured high sensitivity of the method and the results were not affected by temperature, thus the information obtained was accurate and objective. The surface composition of refractory metal samples was studied at room temperature as well as after heating them to a temperature of $800^{o}C$ in a vacuum ($p=10^{-5}$ *Pa*) using a powder medium [4]. The samples under study were made from rolled molybdenum sheets of the *MCH* grade and tungsten of the *TsSDV* grade with dimensions of 30×20×0.5 *mm*. A vacuum furnace was used for refining annealing, and the microhardness was determined using a *PMT* hardness tester.

The obtained results of the X-ray diffraction analysis give grounds to state that unannealed refractory metals (*Mo* and *W*) contain penetrating impurities in the form of graphite – carbon and $MeO_2$ (metal oxide compounds).

Studies on samples of molybdenum and tungsten fractures have shown that the following mass fractions (%) are accumulated in the fracture surfaces at a distance of 10–15 *nm*: in molybdenum the mass fractions are 1.25–1.4 of carbon, 1.15–1.35 of oxygen and 0.35–0.45 of nitrogen, in tungsten the mass fractions are 1.9–2.1 of carbon, 1.2–1.35 of oxygen and 0.4–0.43 of nitrogen. Taking into account the results and data presented in [5], it is possible to consider the distribution of penetration elements in molybdenum and tungsten in surface layers of 1–2 *nm* thickness under the influence of significant pressure, since the crystal lattice in such layers is compressed by almost 10% greater compared to the depths of the metals. To reduce this pressure, the atoms of the penetrating elements come to the surface of refractory metals.

It has been established [6, 7] that in the process of heating and cooling of various metal alloys, their surface layers undergo certain complex technological processes of redistribution of chemical components. A certain part of these components begins to migrate to the surface of the metal-vacuum distribution, another part moves into the depths, and yet another part remains unchanged. The process of cooling the same samples to normal room temperature resulted in the appearance of a reverse return (but not for all of them) to the previous place in the original volume from which the migration during heating occurred. Such behaviour during the migration of chemical elements in metal alloys contributes to a significant deterioration in the performance of materials. Based on the analysis of the findings presented above, the behaviour of carbon, oxygen and nitrogen penetration elements in the process of heating molybdenum and tungsten to $800^oC$ and then cooling them to room temperature was studied.

The investigations revealed that during the first heating ($t$=$150^oC$) of refractory metal samples, the concentration of penetration impurities in molybdenum (Fig. 1) and tungsten (Fig. 2) on the fracture surfaces begins to increase, while in the depth of the metals their content partially decreases.

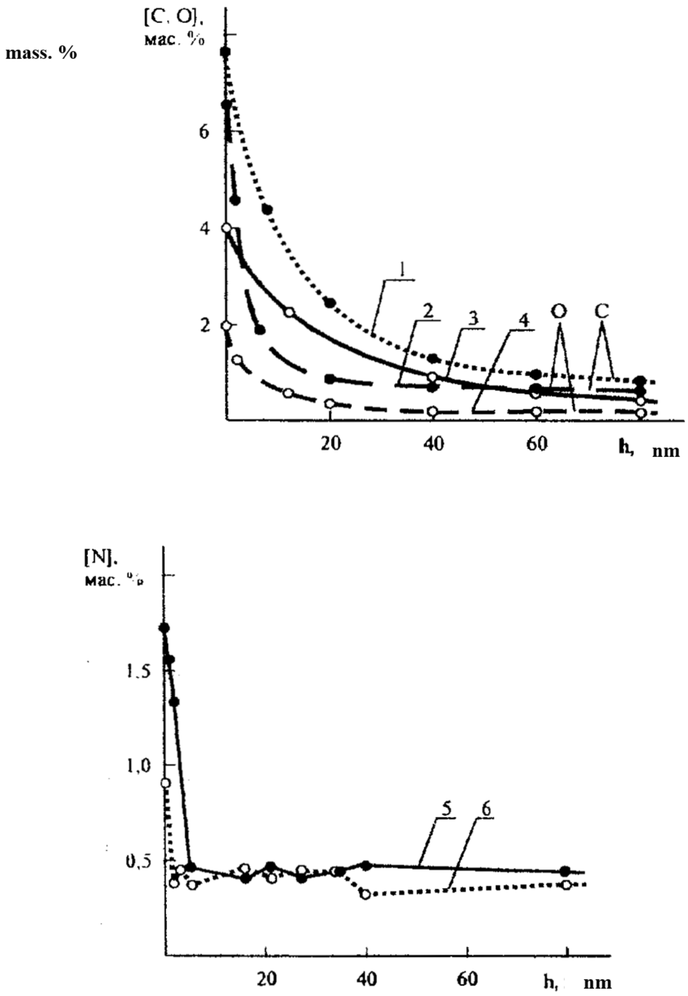


**Figure 1.** Change in the content of carbon, oxygen and nitrogen in molybdenum after the first and second heating followed by cooling to room temperature ($t_{heat}$ – $700\ ^0C$)

The results of the studies showed that molybdenum can contain (%): 1.6–1.8(*C*), 1.3–1.4(*O*), 0.45–0.5(*N*). It should be noted that the concentration of carbon increases rapidly (Fig. 3). It reaches its highest values when the metal is heated in the temperature range of 280–$470^oC$. With the subsequent increase of the temperature the carbon content on the surfaces of the metals under investigation begins to decrease. The second heating of refractory metal samples from room temperature to $700^oC$ practically does not change the concentration of carbon in these samples and it varies within the following range (%): 2.4–2.7 for molybdenum and 1.6–1.8 for tungsten. Heating of molybdenum and tungsten samples to 700$^oC$, followed by cooling, revealed the concentration of oxygen of up to 0.25% on their surface. The studies on the content of oxygen in refractory metals during the second heating showed that its concentration in tungsten decreases by almost twice, and in molybdenum by five times.

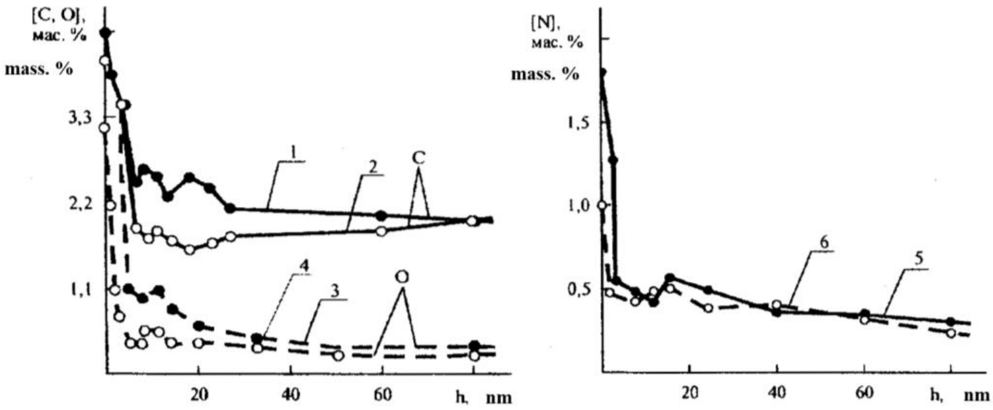


**Figure 2.** Change in the content of carbon, oxygen and nitrogen in tungsten after the first and second heating followed by cooling to room temperature ($t_{heat}$ *– 700 ºC*)

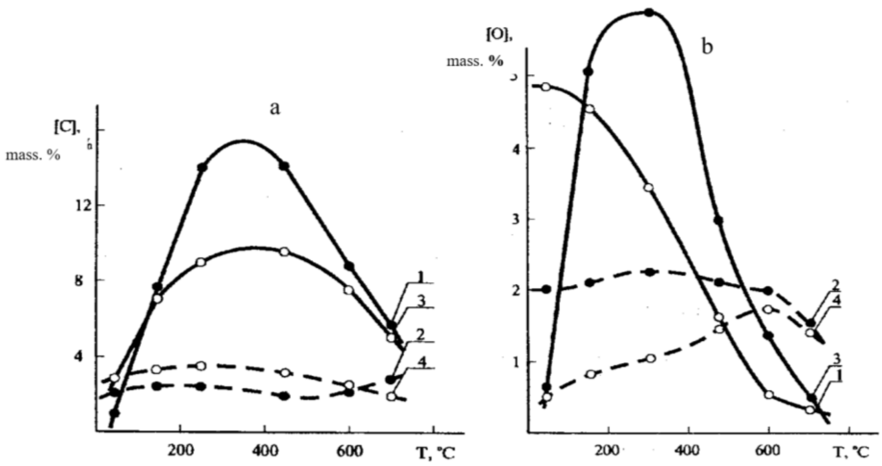


**Figure 3.** The effect of heating temperature on the change in the concentration of carbon (a) and oxygen (b) on the surfaces of molybdenum and tungsten delamination (Mo – ○, W – ●)

Research on the influence of temperature on the loss of specific weight *(Δg*) of molybdenum and tungsten samples during diffusion annealing has shown that the most effective removal of penetration impurities from refractory metals takes place at 500$^oC$. Heating of molybdenum samples in the temperature range of 100–290$^oC$ ensures a maximum specific mass loss in the range of 0.0075–0.0080 $mg/cm^2$, which is 1.1–1.15 (wt%) less for carbon and 0.8–0.9 (wt%) less for oxygen compared to unannealed metal samples. In tungsten samples, the *Δg* value begins to increase at a heating temperature of 277$^oC$., and when the temperature reaches 490$^oC$ , it reaches its highest value (0.0094–0.0098 $mg/cm^2$), which is 1.63–1.69 (wt%) less for carbon and 0.87–0.99 (wt%) less for oxygen compared to unannealed tungsten samples. The refining process does not significantly affect the structure of refractory metals, since the annealing temperature regimes are significantly lower than the recrystallisation temperatures for these metals.

The results of measuring the microhardness of refractory metals were 1750±30 *MPa*, for molybdenum and 2640±70 *MPa*, for tungsten , which is approximately 40% and 30% less than the microhardness of refractory metals that were not subjected to treatment. Subsequent increases in the annealing temperatures of molybdenum and tungsten did not affect the specific weight loss of the samples. Thus, the temperature intervals of diffusion annealing of refractory metals in powder media should vary between 300–500$^oC$, and are important arguments for significant reductions in the temperature regimes of their processing.

The technological process of refractory metals purification can be significantly accelerated by heating molybdenum and tungsten in a pulse mode, which involves heating and cooling. This method of heat treatment of metals is known to stimulate the processes of transferring penetration impurities from the depths of the metal volume to their surfaces. The study of the elemental composition of the fracture surfaces of molybdenum and tungsten samples during their periodic heating to a temperature of 800$^oC$ in a vacuum by Auger electron spectrometry revealed that the first thermal cycle reduces the concentrations as follows: of carbon by 1.80 times, of oxygen by 2.35 times, and of nitrogen by 1.55 times. The second thermal cycle additionally reduces the concentration of penetrating elements by 2.10, 2.80 and 1.70 times, respectively. The obtained results of the studies show that the largest amount of penetration impurities is removed from metals after three thermal cycles.

The study of the dependence of the annealing duration on the surface quality of diffusion purification of molybdenum and tungsten from penetrating impurities showed that five hours of exposure of molybdenum samples to the temperature of 150$^oC$ ensures a decrease in $\Delta g$. Further increases in heat treatment exposures did not significantly affect the change in specific weight. When the annealing temperature is increased to 380$^oC$, a decrease in $\Delta g$ of molybdenum samples is observed, but the duration of the process should be at least five hours. Similar results can be observed for tungsten samples. Diffusion annealing for tungsten samples at a temperature of 280$^oC$ provides a decrease in the specific weight after six hours. Further duration of annealing does not change the specific mass loss of tungsten samples. Increasing the annealing temperature to 450$^oC$ can accelerate the process of removal of penetration impurities.

The results of the study of the atomic structure of grain boundaries make it possible to consider one of the mechanisms for removing penetration components from molybdenum and tungsten. The grain boundaries of refractory metals alternate between grain boundary barriers and free volumes [1, 8]. During the relaxation of internal stresses, some atoms remain in contact with the surrounding atoms and form grain boundary volume-centred polyhedra, which act as barriers to the diffusion process, and there are boundaries with sufficiently free volumes between them. The beginning of diffusion annealing is characterised by the formation of adsorbed monolayers with thermodynamic active elements of powder mixtures on the surfaces of molybdenum and tungsten. During the adsorption of penetrating impurities by the active elements, concentration gradients occur on the surfaces of crystals, and as a result, these impurities diffuse along grain boundaries and accumulate in free zones. Upon reaching a critical concentration, the grain boundary volume becomes permeable and a certain part of the impurities begins to diffuse into the free volumes, where they accumulate to a certain critical concentration, followed by a breakdown of the barrier, and the processes repeat. This constant relay movement removes penetration impurities from the depths of refractory metals at the boundary with powder media, where their adsorption occurs. The studied mechanism can be divided into two stages: the accumulation of penetration impurities and their diffusion through the so-called barrier. This mechanism depends on kinematic factors and the activity of the powder medium [9–15].

Studies of changes in the concentration of penetration elements in molybdenum and tungsten depending on the heat treatment temperature showed that during the first annealing oxygen and nitrogen are removed from refractory metals, and during the second annealing the carbon is removed. The analysis of the values of current mass losses of refractory metal samples showed that the processes of removing penetration elements from molybdenum and tungsten are more efficient during the first heat treatment.

The effectiveness of removing penetration elements from molybdenum and tungsten was evaluated by using the plasticity of metals, which ensures the ability of refractory metals to be shaped. The plasticity coefficient was the number of bends of molybdenum and tungsten samples with dimensions of 30×20×0.5 *mm* at 90º. According to the standard, the bending of rectangular samples at 90º ˚ and their return to their original position was considered as one bend. The studies showed that after the first diffusion annealing, the plasticity coefficient of molybdenum increased by 3–4 times and that of tungsten by 2–3 times compared to untreated refractory metal samples. The second diffusion annealing changed the plasticity coefficients as follows: for molybdenum 12±2 bends, for tungsten 5±1 bend, which is 4–5 times higher than for untreated refractory metal samples.

## 4. CONCLUSIONS

Thus, the two-stage treatment of molybdenum and tungsten in a vacuum environment using active powder mixtures provides effective removal of harmful penetration impurities, which results in a significant increase in the plasticity of refractory metals*(Mo* and *W*).

**References**

1. Bochar I. Y., Loskutov V. F., Khizhnyak V. G., Pogrebova I. S., Horbatyuk R. M. Carbide coatings on steels and hard alloys: monograph. Ternopil: Lileya, 1998. 144 p. [In Ukrainian]
2. Kovbashyn V., Bochar I. Investigation of the change in technological properties of refractory metals after diffusion saturation. Scientific Journal of the Ternopil National Technical University: TNTU, no. 1 (109), 2023, pp. 121–129. https://doi.org/10.33108/visnyk_tntu2023.01.121
3. Buketov A., Stukhlyak P., Maruschak P., Panin S., Menou A. Regularities of impact failure of epoxy composites with $Al_2O_3$ microfiller and their analysis on the basis of external surface layer concept. Key Engineering Materials, 712, 2016, pp. 149–154. https://doi.org/10.4028/www.scientific.net/KEM.712.149
4. Fedoreiko V. S., Lutsyk I. B., Iskerskyi I. S., Zagorodnii R.I . Increase of energy efficiency of heat generator through batching components of burning. Naukovyi Visnyk Natsionalnoho Hirnychoho Universytetu, 2014, (4), pp. 27–32.
5. Horbatyuk R. M. Surface hardening of molybdenum and tungsten. Mechanical engineering. Lviv, no. 1, 2000, pp. 14–18. [In Ukrainian]
6. Bochar I. Y., Dziadykevich Yu. V., Smiyan O. D., Horbatyuk R. M. Method of processing molybdenum and tungsten and their alloys (patent), no. 30238 A dated November 15, 2000 Bull, no. 6–11. [In Ukrainian]
7. Leonid G. Kozlov, Leonid K. Polishchuk, Oleh V. Piontkevych, Roman. M. Horbatiuk, Mykola P. Korinenko, Paweł Komada, Sandugash Orazalieva, Olga Ussatova. Experimental research characteristics of counterbalance valve for hydraulic drive control system of mobile machine. Przegląd elektrotechniczny. ISSN 0033-2097, R. 95, Vol. 2019. No. 4. pp. 104–109.
8. Kovbashyn V., Bochar I. Method of reaction-sintered products processing based on silicon carbide and molybdenum disilicide. Scientific Journal of the Ternopil National Technical University. Ternopil: TNTU, no. 2 (94), 2019, pp. 75–79. https://doi.org/10.33108/visnyk_tntu2019.02.075
9. Sosnovsky P. A., Epik A. P. The use of activators in the process of diffusion contact saturation of metals in powders. Protective high-temperature coatings. Lviv, Nauka, 1972, pp. 22–23. [In Ukrainian]
10. Kovbashyn V., Bochar I. The study of technological peculiarities for improvement of chemical and physico-mechanical properties of reaction-sintered ceramic materials based on molybdenum disilicide. Scientific Journal of the Ternopil National Technical University. Ternopil: TNTU, no. 2 (106), 2022, pp. 39–46. https://doi.org/10.33108/visnyk_tntu2022.02.039
11. Bochar I., Horbatyuk R. Increasing the plasticity of molybdenum and tungsten. Bulletin of the Ternopil State Technical University, 2000, vol. 5, no. 1, pp. 16–20. [In Ukrainian].
12. Bochar I. Y., Dzyadykevich Y. V., Horbatyuk R. M. The composition of the mixture for boronizing products from silicon carbide and molybdenum disilicide (patent), no. 30237 A dated November 15, 2000 Bull, no. 6–11. [In Ukrainian].

13. Bochar I. Y., Dzyadykevich Yu. V., Horbatyuk R. M. The composition of the mixture for silicification of silicon carbide and molybdenum disilicide products (patent), no. 30239 A dated November 15, 2000 Bull, no. 6–11. [In Ukrainian].
14. Bochar I., Horbatyuk R. Influence of activators on the process of diffusion saturation of SiC and $MoSi_2$ with silicon and boron. Bulletin of the Ternopil State Technical University, 2002, vol. 7, no. 1, pp. 19–26. [In Ukrainian].
15. Bochar I., Horbatyuk R. Properties of the protective composition applied to the surface of ceramic materials. Scientific Notes Series: Engineering Mechanics. Lutsk: LNTU, no. 24, 2009, pp. 21–28. [In Ukrainian]

**УДК 668.045.18**

# ТЕРМІЧНА ОБРОБКА МОЛІБДЕНУ І ВОЛЬФРАМУ В ПОРОШКОВИХ СЕРЕДОВИЩАХ

**Василь Ковбашин[1]; Ігор Бочар[2]**

*[1]Тернопільський національний технічний університет імені Івана Пулюя, Тернопіль, Україна*
*[2]Тернопільський національний педагогічний університет імені Володимира Гнатюка, Тернопіль, Україна*

***Резюме.*** *Описано рекомендовані шляхи покращення технологічних та фізико-механічних властивостей тугоплавких металів (молібдену та вольфраму) після дифузійного відпалювання у кілька етапів. Для значного підвищення технологічних характеристик і переходу на жорсткіші умови експлуатації виробів із тугоплавких металів необхідне вдосконалення уже існуючих способів обробки металів та внесення суттєвих змін у розроблення нових. Досліджено та проаналізовано різні напрями обробки тугоплавких металів, які передбачають процес нагрівання й охолодження металів. При цьому їхні приповерхневі шари отримують певні складні технологічні процеси перерозподілу хімічних компонентів. Певна частина починає мігрувати на поверхню розподілу метал-вакуум, інша частина переміщається в глибину, а ще одна частина залишається без переміщень. Вивчено поведінку елементів проникнення вуглецю, кисню та азоту при нагріванні молібдену та вольфраму до температури 800ºC з наступним охолодженням до кімнатної температури. Для оцінювання змін механічних властивостей молібдену і вольфраму після дифузійного відпалювання проведено відповідні випробування. Для вивчення змін технологічних та фізико-механічних властивостей у тугоплавких металів після процесу дифузійного відпалювання в активному порошковому середовищі проведено випробування на згинання й перегинання. Проведені дослідження на вміст кисню у тугоплавких металах при другому нагріванні показали, що його концентрація у вольфрамі зменшується майже у два рази, а у молібдені – у п'ять разів. Технологічний процес очищення тугоплавких металів можна суттєво пришвидшити, якщо провести нагрівання молібдену і вольфраму в імпульсному режимі, який передбачає нагрівання-охолодження. Як відомо, даний спосіб термічної обробки металів стимулює процеси перенесення домішок проникнення з глибини об'єму металів на їх поверхні. Встановлено, що після першого дифузійного відпалювання коефіцієнт пластичності молібдену підвищувався у 3–4 рази, а вольфраму – у 2–3 рази в порівнянні з необробленими зразками тугоплавких металів. На основі аналізу літературних даних і проведених досліджень запропоновано комплекс заходів, направлених на покращення технологічних та фізико-механічних властивостей тугоплавких металів (молібдену і вольфраму) після дифузійного відпалювання в активному порошковому середовищі.*

***Ключові слова****: молібден, вольфрам, пластичність, термічна обробка.*

*https://doi.org/10.33108/visnyk_tntu2024.03.023* *Отримано 21.07.2024*