Investigation of the influence of modification of the working tool for the manufacture of niobium case products

E Yu Remshev\textsuperscript{1,7}, Z N Rasulov\textsuperscript{1}, S A Voinash\textsuperscript{2}, V A Sokolova\textsuperscript{3}, I A Teterina\textsuperscript{4}, V N Malikov\textsuperscript{5} and T N Vagizov\textsuperscript{6}

\textsuperscript{1}Baltic State Technical University “Voenmeh”, 1st Krasnoarmeyskaya, 1/21, Saint Petersburg, 198005, Russian Federation
\textsuperscript{2}PRO FERRUM Limited Liability Company, 1st Krasnoarmeyskaya, 1, St. Petersburg, 198005, Russian Federation
\textsuperscript{3}Saint Petersburg State Forest Technical University named after S.M. Kirov, 5, Institutskiy per., St. Petersburg, 194021, Russian Federation
\textsuperscript{4}Siberian State Automobile and Highway University (SibADI), 5, Mira ave., Omsk, 644080, Russian Federation
\textsuperscript{5}Altai State University, Lenina, 61, Barnaul, 656049, Russian Federation
\textsuperscript{6}Kazan State Agrarian University, 65, Karla Marksa str., Kazan, 420015, Russian Federation
\textsuperscript{7}E-mail: Remshev@mail.ru

Abstract. The main production of machine-building enterprises of various industries is the production of metal parts and products, 90-95\% of which are manufactured using metal processing by pressure. Ensuring the stability of the technological processes of cold stamping is impossible without the use of interoperative coatings, which play the role of lubrication, preventing the diffusion “setting” (interpenetration at the atomic-molecular level) of the processed materials and tools. Therefore, one of the tasks in constructing the technology for manufacturing parts from these materials is to conduct a test cycle to establish the most acceptable coatings at the intermediate stages of processing. In the process of studying the operability and manufacturability, it is also advisable to use new methods for evaluating quality indicators at separate stages of processing semi-finished products and at the stages of control of finished products, which allows practically eliminating defects due to internal defects, ensuring the uniformity of the microstructure and predicting the operability of finished products during operation. Ensuring the quality of stamped semi-finished products made of refractory metals (niobium, molybdenum) is an urgent task due to the significant proportion of defects during cold stamping of these parts.

1. Introduction

The main group of refractory metals are tungsten, rhenium, tantalum, molybdenum and niobium, additional metals include titanium, vanadium, chromium, zirconium, ruthenium, rhodium, hafnium, osmium and iridium. We will highlight the main areas of use of components and structures made of refractory metals and alloys: heat-resistant and corrosion-resistant alloys for oil refining equipment; superconductors for radio electronics; jet engines; acid-resistant alloys for chemical equipment; compact capacitors; parts of electronic lamps; for bonding bones and nerves.
Products that are made of rare-earth, refractory metals (niobium, tantalum, titanium alloys, etc.) are used. Parts made of niobium and molybdenum serve as screens that emit energy pulses, non-magnetic housings, flexible elements, etc. A wide range of hollow axisymmetric parts made of niobium and molybdenum are manufactured using cold stamping processes. The production of semi-finished products by cold stamping from refractory materials by traditional methods causes certain difficulties, which is accompanied by a significant proportion of defects (up to 50%). The cause of defects during deformation is the action of stresses of these materials, due to the action of rigid stress state schemes that are implemented in the process of sheet stamping. An important factor in reducing the technological properties and stampability of the material is the physical features of refractory metals, such as adhesion to the tool and structural changes of the material depending on the degree of deformation and the effect of residual stresses [1-5].

2. Materials and methods

Figure 1, a shows the graphical dependence of the change in the annealing temperature of a refractory metal (niobium), depending on the presence of certain impurities in its composition. The content of molybdenum (Mo) more than 3% increases the annealing temperature of 1200 °C, and the content of boron B from 0.8 to 1% reduces the annealing temperature to 1030-1000 °C. The titanium content from 5 to 5.5% also reduces the annealing temperature to 1070-1090 °C. The change in the annealing temperature in the range from 1050 °C to 1200 °C, which is essential for the production of products in the working conditions of the enterprise. Surface defects leading to cracks (figure 1, b) are observed during stamping, both at the first operation (convolution) and at subsequent extracts. The nature of the structure and, first of all, the grain size, as well as the state of the metal, have a great influence on the mechanical properties and deformability of niobium during pressure treatment. A significant change in the structure, consisting in the crushing of grains and the appearance of the niobium texture in the recrystallized state, is observed after deformation of 25-60% (table 1).

| Vickers hardness (kg s/mm²) | 0   | 10  | 20  | 30  | 40  | 50  | 60  |
|----------------------------|-----|-----|-----|-----|-----|-----|-----|
| Level of deformation       | 84  | 104 | 113.5-118.5 | 119-128.5 | 123-136.5 | 128-142 | 132-148 |

Based on the above data, it follows that the hardness of niobium increases with the degree of deformation to 25% and changes slightly in the range of 25-60%. When the deformation is more than 60%, the hardness increases again. The main type of heat treatment of niobium and most of its alloys is annealing, which is produced mainly in vacuum furnaces with metal heaters and less often in an atmosphere of neutral gases. The vacuum should not be lower than 10⁻⁵-10⁻⁴ mm Hg. The listed features of niobium, despite its high plasticity, lead to a number of technological problems when implementing cold stamping technology in the production of hollow axisymmetric parts: a significant proportion of defects (up to 50%); the inexpediency of interoperative annealing, due to significant changes in the properties of the metal during cold stamping; high adhesion to the tool, and as a result, rapid wear; the impossibility of operational control of the source material and semi-finished products during successive cold stamping operations. These problems lead to a decrease in labor productivity and an increase in the cost of manufacturing products.
Figure 1. Features of cold stamping of niobium. a - change in the annealing temperature of niobium depending on the content of impurities; b - hollow axisymmetric parts made of molybdenum and niobium.

The use of a hood with thinning of the wall will increase the manufacturability of the product, as well as intensify the production process. Under the manufacturability of the parts obtained by sheet stamping, it is necessary to understand such a combination of the main elements of its design, which provides the simplest and most economical production of the part in compliance with the technical and operational requirements for it. A mandatory point after each stamping operation is the degreasing of the workpiece to obtain the necessary dimensions and quality of the part. In order to make this product, it is required to cut the sheet into strips, and then, using the cutting operation, we get a blank in the form of a circle. Next, we apply 1-5 operations of drawing without thinning and 1-5 operations of rotary drawing with thinning, and after crimping the muzzle part. Then the operation of cutting the bottom and the electroerosive method of obtaining holes is applied.

The aim of the work is to study the metal damage of stamped semi-finished products made of niobium in the technology of cold stamping of hollow axisymmetric parts using the extraction process and to develop practical recommendations for improving the quality of stamped parts. The objectives of this research work are an experimental study of the physical, mechanical and technological properties of niobium in the process of cold stamping of the "screen" part, an assessment of the damage to the metal of semi-finished products during the operations of the technological process, as well as a study of the influence of the modification of the working tool for stamping semi-finished products from niobium on the quality of stamped parts, establishing the regularities of the influence of technological factors on the quality of stamped semi-finished products and the damage to the metal. To assess the degree of suitability of the screen design for its production by drawing methods while ensuring the stability and strength of the workpiece during deformation to obtain a given level of quality of the stamped part, a study was planned and conducted based on the results of tensile testing of flat samples made of niobium NBPL-1 in the initial state, after interoperative vacuum annealing, as well as after coating with organofluorine nanocomposition. The test (stretching) was performed on a universal testing machine (figure 2) SHIMADZU AGX-100 kN (Center for Collective Use "Center for Materials Research" of the Baltic State Technical University "VOENMEH" named after D. F. Ustinov), chemical analysis of the material showed that the content of Nb 98.75\% (±0.165), impurities P 0.97\% (±0.027), Sb 0.22\% (±0.049), Mo 0.06\% (±0.014).
3. Results

The results of the experimental study are presented in Table 2.

Based on the results of the experimental study, a graphical interpretation of the changes in the mechanical characteristics of niobium NBPL-1 depending on the state (initial state, recrystallization annealing, organofluorine coating) is constructed. In the initial state, the plasticity is $\delta = 8-10\%$, in the part of the NBPL-1 stretching diagram of the neck formation area, the deformation partially passes through a brittle mechanism (areas of vertical load drop).

Table 2. Results of mechanical tensile tests of samples of niobium NBPL-1 with a thickness of 0.15 mm (the starting material for the manufacture of the screen).

|                     | $\sigma_{0.2}$ MPa | $\sigma_B$ MPa | $\delta$ % |
|---------------------|--------------------|----------------|------------|
|                     | Original 1250 °C    | Fluoro-surfactant coating | Original 1250 °C | Fluoro-surfactant coating | Original 1250 °C | Fluoro-surfactant coating |
| 142                 | 300                | 120            | 220        | 405           | 221           | 8.5         | 8          | 7.5          |
| 145                 | 320                | 130            | 223        | 400           | 217           | 10          | 10         | 9           |
| 147                 | 345                | 160            | 225        | 403           | 221           | 9           | 8          | 8.5          |
| 142                 | 335                | 155            | 220        | 395           | 228           | 10          | 9          | 9           |
| 143                 | 355                | 147            | 218        | 396           | 227           | 9           | 10         | 9           |
| 145                 | 360                | 149            | 223        | 405           | 226           | 9           | 8          | 8           |
| 150                 | 365                | 158            | 225        | 400           | 225           | 10          | 10         | 8.5          |
| 150                 | 370                | 160            | 220        | 398           | 215           | 8.5         | 10         | 9           |
| 152                 | 376                | 157            | 225        | 400           | 220           | 10          | 9          | 9           |
| 152                 | 376                | 130            | 223        | 405           | 210           | 9           | 8          | 8.5          |
| 149                 | 370                | 145            | 220        | 401           | 205           | 10          | 10         | 9           |
| 150                 | 370                | 140            | 220        | 397           | 228           | 8.5         | 8          | 8           |
| 152                 | 372                | 155            | 223        | 406           | 220           | 9           | 9          | 9           |
| 152                 | 370                | 155            | 220        | 400           | 200           | 9           | 10         | 9           |
| 149                 | 370                | 160            | 225        | 399           | 228           | 10          | 10         | 8           |

The coating application has almost no effect on the plasticity of the NBPL-1 material in the initial state. When the samples are coated with organofluorine and then stretched, the neck formation area is shown in part of the diagram, there are fewer zones with brittle fracture, but the plasticity is lower than in the initial state, the time to destruction of the samples is less. The surface properties are determined.
by the method of measuring the wetting edge angle and determining the free surface energy. The device for measuring the edge angle of wetting DSA-25E allows you to analyze the shape of a liquid drop on the surface of a solid. Drop shape analysis is an image analysis method for determining the edge angle and/or surface / interfacial tension. A drop of liquid is applied to a solid surface, after which the image is recorded using a camera and transmitted to a program for analyzing the shape. In the process of recognizing the contour of a drop, based on a black-and-white image, a geometric model of the contour of a drop is selected in accordance with figure 3. The edge angle determines the wettability of a solid surface with a liquid and allows you to calculate the free energy of the surface using one of the available methods: Zisman, Fawkes, OVRK, Wu, Schultz, as well as Ossa-Hood. Comprehensive studies of the structure and properties of thin-film coatings of non-metallic materials have shown that, regardless of the molecular structure, stable films form, the adsorption activity of the surface layers. It is known that the tribological properties of friction units are largely determined by the value of their surface energy and the ratio of its dispersion and polar components of the processed material.

![Figure 3](image_url)

**Figure 3.** The results of determining the wetting angle on the device for measuring the wetting edge angle DSA-25E. a - the results of measuring the wetting angle on the surface of the working tool with methane diiode of the tool without surface modification; b - the results of measuring the wetting angle on the surface of the working tool with distilled water of the tool without surface modification; c - the results of measuring the wetting angle on the surface of the working tool with methane diiode after surface modification; d - the results of measuring the wetting angle on the surface of the working tool with distilled water after surface modification.

As part of the experimental study, the working surfaces of the tool for making a screen made of niobium were modified. Stamping was carried out in experimental dies without modification of the tool surface and with modification of an active lubricating coating based on an organofluorine nanocomposition. The main transitions for the study were cutting-folding and subsequent extraction of semi-finished products. The experimental stamp (double stamp) of the cutting-convolution is shown in figure 4. During the experimental study of metal damage at the stamping transitions, cutting-convolution
and subsequent extracts were carried out in experimental dies in the laboratory, at the first stage the tool was not modified, at the second stage the working surface of the matrices and punches was modified with an active lubricating coating based on an organofluorine nanocomposition.

4. Discussion

The analysis and evaluation of the effect of an active lubricating coating based on organofluorine nanocomposition was carried out for the possible effect of tool modification on the material. According to the results of the tensile tests of the coated samples, no changes in the mechanical characteristics were detected compared to the initial state. In some cases, there is not a significant increase in microhardness.

One of the mechanisms explaining the effect of increasing the microhardness of metal substrates treated with an active lubricating coating based on an organofluorine nanocomposition may be that the oligomer molecules “flow” into the print after the indentorization of the material under study has been extracted, resulting in a decrease in the diagonal of the print and, as a result, an increase in the calculated value of microhardness. To confirm or refute this assumption, experiments were conducted to determine the microhardness of coated metals and after removing the fluorine-containing coating from the metal surface. To do this, the fluorinated oligomer was removed from the sample surface using a solution of hladon 113 and the microhardness of metals was measured. The conducted studies have shown that the
removal of the oligomer from the surface does not actually affect the results of measurements of microhardness values (figure 5).

![Figure 5. Dependence of the microhardness of metal substrates (1) treated once with an active lubricating coating (2) and after removing the coating from the metal surface with hladon 113 from the metal surface (3).](image)

Thus, fluorinated oligomers will strengthen the surface layers of the metal, if chemical (chemisorption) bonds are formed between the film of the fluorinated oligomer and the metal. If the formation of a chemisorption interaction between the oligomer molecules and the metal does not occur, the surface layers of polycrystals are plasticized. Energy treatment intensifies the processes of crystal formation in thin films, as a result, the microhardness of the thin-layer composite coating also increases.

After interoperative vacuum annealing, the plasticity of NBPL-1 does not change significantly, and the strength characteristics increase, which can lead not only to the appearance of defects during the plastic deformation operation, but also to reduce the deformation rate. An increase in the rate of deformation under static tension affects the forming structure as well as a decrease in temperature. During vacuum heat treatment, hardening and softening processes occur (dynamic and thermal return). The results obtained are consistent with the works of other authors. The authors point out that the transition temperature is influenced by many factors, the most important of which are the chemical composition, the structure of the material, the rate of deformation, the type of stress-strain state [6]. However, the recommendations given in the literature on niobium sheet stamping do not, as a rule, contain any instructions on the composition of the material under study, on its structure, etc.

5. Conclusion
The analysis of the features of stamping of refractory materials and applied technical solutions in the field of quality improvement and automation of the process is carried out. Mechanical tensile tests of NbPi-1 niobium samples were carried out in the initial state, after classical annealing, as well as when coated with an organofluorine nanocomposition. The analysis of the results of mechanical tests allowed us to establish the true values of mechanical properties. The regularities of the influence of the surface characteristics of the working tool are established and a method of experimental research is developed to assess the destruction of materials from the action of mechanical loads and the external environment, to study the influence of the modification of the working tool for stamping semi-finished products from niobium on the quality of stamped parts, to establish the regularities of the influence of technological factors on the quality of stamped semi-finished products and the damage to metal.

References
[1] Gusev A I 2016 Petrology, geochemistry and ore content of anorogenic granitoids of the shibeliisky complex of the Gorny Altai Bulletin of the Tomsk Polytechnic University Geo Assets Engineering 327(6) 71-82
[2] Botashev A Yu and Bayramukov R A 2018 Development and research of a device for gas sheet stamping with a piston pressure multiplier Bulletin of Samara University Aerospace Engineering Technology and Engineering (Vestnik Samarskogo universiteta Aerokosmitcheskaya tekhnika, tekhnologii i mashinostroyenie) 2(2) 44-51
[3] Minko D V 2020 Analysis of the prospects of the application of the electroplastic effect in the processes of processing metals with pressure Foundry production and metallurgy 4(2) 125-30
[4] Troickij O A 2018 Electroplastic effect in metals Ferrous metallurgy Bulletin of scientific
technical and economic information 9 65-76

[5] Makeyev A B, Krasotkina A O and Skublov S G 2016 Geochemistry and U-Pb age of zircon from Pizhenskoe titanium deposit (Middle Timan) Vestnik IG Komi SC UB RAS 5 38-52

[6] Bespalov D A, Remshev E Y, Danilin G A, Vorob’eva G A and Pekhov V A 2018 Influence of Heat Treatment on the Properties of Nickel–Chromium–Silicon Bronze Wire Russian Engineering Research 38(1) 29-32