DEVELOPMENT AND CHARACTERIZATION OF NEW BIOMEDICAL ALLOYS BASED ON NiCrMo AND NiCrMoTa

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In the present work, we proposed the development of a new type of biomedical alloy - NiCrMoTa with improved structural properties compared to the basic NiCrMo alloy. The studied alloys were obtained by melting in a vacuum melting furnace in a neutral atmosphere and were characterized chemically and microstructurally through X-ray fluorescence spectrometry (XRFS), optical microscopy, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). These techniques highlighted the microstructures and elemental compositions of the NiCrMo and NiCrMoTa alloys.

Keywords: biomedical alloys; tantalum; NiCrMo; NiCrMoTa; XRFS, SEM-EDX

1. Introduction

Bone health issues remain a major concern in many countries, but tissue engineering and regenerative medicine offer hope for the future. Improving the materials used in bone replacements and finding new alternatives are essential. Although pure titanium and its alloys are considered the best metallic biomaterials for this purpose due to their biocompatibility, they are not without flaws.

Metallic materials used in implantology must be biocompatible and meet certain requirements, such as corrosion and wear resistance, mechanical strength, and elastic modulus [1]. In addition to biological safety, the design of medical devices plays an important role in their biocompatibility. The problems encountered with metallic implants sometimes include mechanical aspects, not just material-related issues.

NiCrMo-based alloys [2-4] are chosen in the medical industry for the manufacturing of surgical implants and medical instruments for several objective reasons. Overall, the use of NiCrMo-based alloys in the medical field contributes to the development of advanced, durable, and reliable medical components that

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improve patients' quality of life and enable more efficient and safer surgical procedures.

Additionally, NiCrMo-based alloys are also valued in the medical field for their ability to be effectively sterilized. Sterilization is crucial for preventing infections and other complications during surgical procedures or in the use of medical instruments. NiCrMo-based alloys can withstand various sterilization methods, such as steam sterilization, ethylene oxide sterilization, or radiation sterilization, without losing their structural integrity or mechanical properties. These alloys are also versatile and can be processed into various shapes and sizes, allowing the production of customized implants and surgical instruments tailored to the individual needs of patients [5-7]. This ability to customize is essential for optimizing medical treatment outcomes and improving the patient recovery process [8, 9].

We aimed to develop new biocompatible alloys with superior properties to those already existing. Among the wide range of biocompatible materials, tantalum presents particular interest due to its biocompatibility and corrosion resistance [10-12]. Tantalum is used in the manufacture of orthopedic implants, such as screws, plates, and joint prostheses. It is also used in cardiac stents and in the manufacture of heart valves due to its biocompatibility and stability within the body's internal environment. It is employed in the reconstruction of craniofacial bones due to its malleability and its ability to integrate well with bone tissue. The electrical properties of tantalum make it suitable for use in electrodes for neural stimulation and other electro-medical applications [13-15]. It is successfully used in various dental applications, including crowns and dental bridges. The use of tantalum in biomedicine has three main advantages: chemical inertia, osteoconductivity, and versatility. Tantalum does not react with body fluids, minimizing the risk of allergic or inflammatory reactions. It can promote bone growth around implants, ensuring better fixation. It can be utilized in a variety of forms and structures, including in complex devices.

2. Materials, methods and experimental procedures

To achieve the proposed objective, namely the development of new biocompatible alloys for medical applications, the alloying element Ta was selected, starting from a known biocompatible binary alloy Ni70-Cr20-10Mo. The characteristics of the elemental metallic materials are presented in Table 1. These are in bulk form with high purity. The development of the proposed alloys was carried out using a LEYBOLD-HARAEUS IS-1-SP induction furnace, with a nominal voltage of 380 V (HAREUS GmbH, Hanau, Germany), with a capacity of 200g – 1000g per batch, in a protective argon atmosphere (sample preparation location: INCDIE ICPE-CA, Laboratory of Magnetic Materials and Applications).

Table 1

Characterization of the elemental materials that are components of the selected biomedical alloys

Element	Density (g/cm^3)	Melting temp. / Melting point (°C)
Ni	8.9	1455
Cr	7.15	1907
Mo	10.28	2623
Ta	16.69	3020

The maximum operating temperature of the furnace is 1800°C. Melting was performed in ceramic crucibles. The ISP-1 Leybold - Heraeus vacuum melting furnace provides the capability for rapid cooling during alloy solidification, as well as temperature control of the alloy and operation in a neutral atmosphere (argon with 99.995% purity) or reducing atmosphere (purified and dried hydrogen) at a pressure no greater than 1 atm.

Fig. 1 shows the process of obtaining the material in ceramic crucibles. The alloying is performed by induction in the ceramic crucible, with the obtained melt being either poured into copper molds or drawn into quartz rods using a pump.

Fig. 1. Image obtained during the induction melting process

The compositions and proportions selected for each type of material developed are presented in Table 2. Each material was produced in batches of 200 g, from which both cylindrical samples with a diameter of approximately 38 mm and a height of approximately 14 mm, as well as bars with a diameter of 5 mm and variable lengths, were made. To obtain the samples from Fig. 2, a temperature of approximately 1800°C was required, with a hold time of 5 minutes for melting all the materials, followed by a 2-minute hold time for homogenization. To evaluate the microstructural aspects and chemical homogeneity of the alloys obtained after the melting and casting, the materials were examined using SEM-EDS (Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy) to determine the distribution of the alloying elements within the alloy matrix.

Table 2

Compositions and proportions selected for each type of material developed

Sample code	Constituent Elements	wt. %	Mass (g)
P1-NiCrMo	Ni	70	140
	Cr	20	40
	Mo	10	20
P2-NiCrMoTa	Ni	65	130
	Cr	20	40
	Mo	10	20
	Ta	5	10

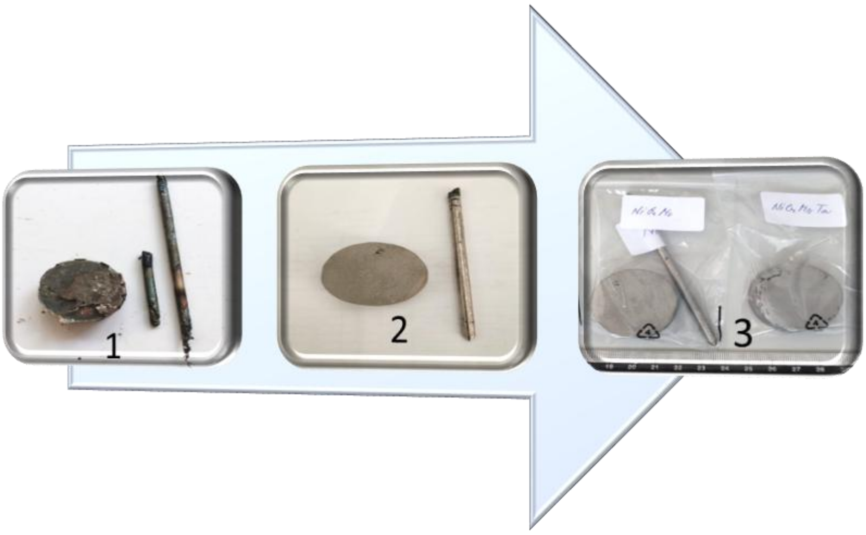


Fig. 2. The NiCrMo and, NiCrMoTa alloys obtained by induction melting in the form of discs and bars before and after preparation

To be subjected to qualitative microscopic analysis, the samples were embedded in phenolic resin, according to the PTL PRG procedure. After embedding, surface preparation was carried out. The surface preparation method involved grinding with abrasive paper and polishing with Lecloth fabric soaked in a suspension of α-alumina in water, according to the PTL PRG procedure. After grinding, the samples were subjected to electrochemical etching (etching solution: acetic acid, HNO_3, water). The equipment used included a polarized light microscope of the AxioImager A1m type, with AxioVision Release 4.8 software. Image capture was performed with a Canon Power Shot A 640 digital camera, Digital Zoom 10X (magnification range X180, X900, measurement precision - Magnification X90-X900).

The obtained samples shown in Fig. 2 were also analyzed by XRFS (X-ray Fluorescence Spectroscopy using the TurboQuant-Alloys analytical software of the XEPOS spectrometer (SPECTRO Analytical GmbH).

3. Results and discussion

The concentrations of the elements identified by TurboQuant-Alloys software are presented in Tables 3 for sample P1-NiCrMo and Table 4 for sample P2-NiCrMoTa. The purity of the alloys is crucial in the industry, as impurities such as P, Si, Fe, etc., can negatively affect the quality of the products.

Table 3

XRFS Analysis Report for Sample P1-NiCrMo

Symbol	Element	Normalized Intensity	Concentration (%)	Abs. Error
Cr	Chromium	10175.14	**20.01**	0.02
Ni	Nickel	47612.29	**68.93**	0.06
Mo	Molybdenum	745.26	**10.02**	0.01
Other elements		<0.0001	**<0.77**	(0.0)
	Sum		**100**	

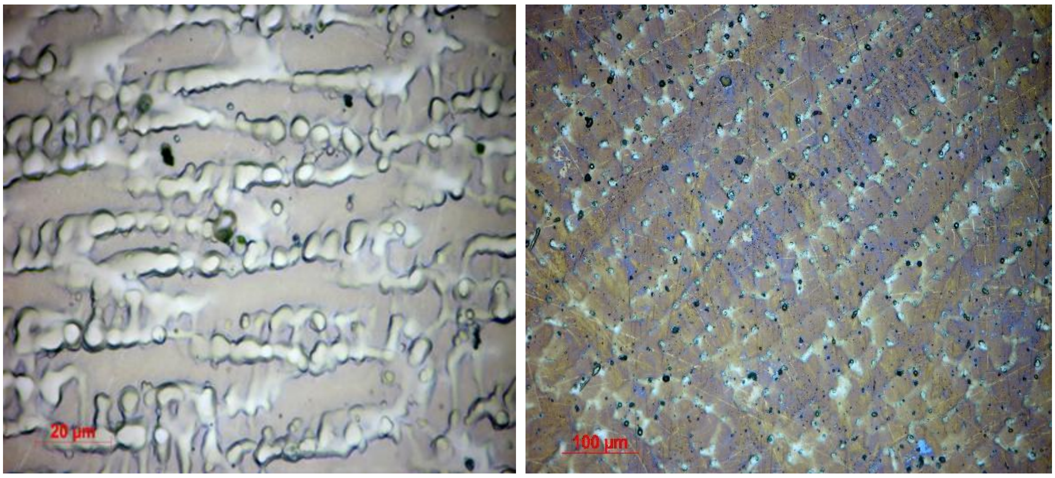
Table 4

XRFS Analysis Report for Sample P2-NiCrMoTa

Symbol	Element	Norm. Int.	Concentration (%)	Abs. Error
Cr	Chromium	10436.13	**19.987**	0.02
Ni	Nickel	38645.52	**64.87**	0.065
Mo	Molybdenum	654.89	**10.013**	0.01
Ta	Tantalum	112.16	**5.001**	0.005
Other elements		<0.0001	**0.129**	(0.0)
	Sum		**100**	

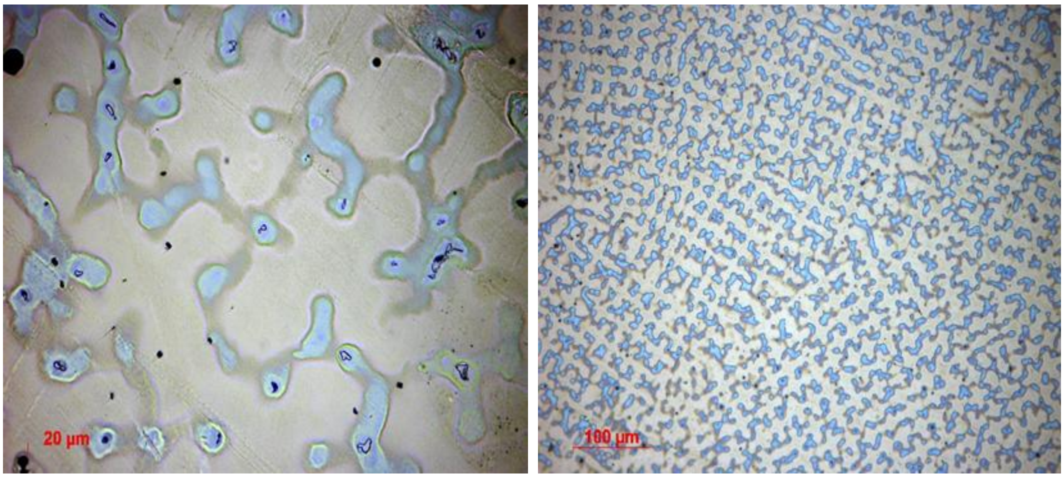
The results in Tables 3 and 4 confirm the achievement of the planned alloys, meeting very tight tolerances for the three base elements.

After determining the element concentrations in the obtained samples, a metallographic analysis was performed using an optical microscope to visualize fine structures and details of the samples. The samples were metallographically prepared before microscope examination to reveal the material's structure. The images in Figs. 3 and 4 show the microstructures of the cast alloys – P1-NiCrMo and P2-NiCrMoTa, using two different magnifications. The micrographs illustrate the variation in the microstructure of each sample as the alloying element differs.



(a) **(b)**

Fig. 3. Optical microstructures of the P1-NiCrMo alloy sample: a) magnification X900, scale 20 μm and b) magnification X180 scale 100 μm

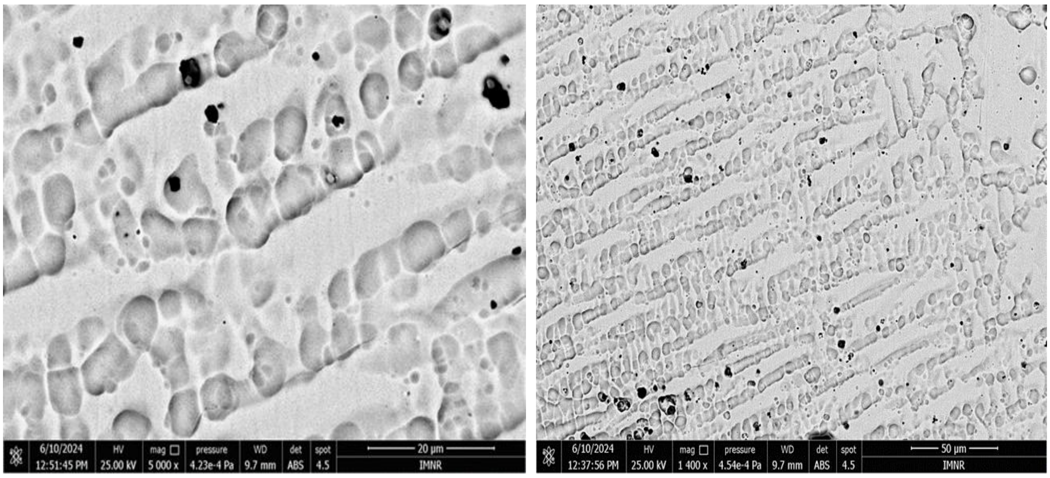


(a) **(b)**

Fig. 4. Optical microstructures of the P2-NiCrMoTa alloy sample: a) magnification X900, scale 20 μm and b) magnification X180 scale 100 μm

All phases are uniformly distributed in the structure of the produced alloys, without the appearance of conglomerates or clusters that could cause heterogeneity in the chemical composition. The resulting structures are multiphase, very fine and uniformly distributed. Ensuring a uniform distribution of all phases within NiCrMo and NiCrMoTa alloy is critical to maintaining consistent chemical composition and properties throughout the material. This homogeneity prevents the formation of conglomerates or clusters, which could lead to weak points or inconsistencies.

The samples were also subjected to SEM-EDS analysis. The microstructural analysis of the alloys samples evaluates the microstructure and phase distribution of alloying element after the solidification process. Figs. 5 and 7 show SEM images of the two samples - P1-NiCrMo and P2-NiCrMoTa, where it can be observed that the distribution is homogeneous, the size and morphology of compounds are uniform, no agglomeration of particles is detected. Figs. 6 and 8 show the EDS analysis spectra for the two samples - P1-NiCrMo and P2-NiCrMoTa.



(a) **(b)**

Fig. 5. SEM image of the P1-NiCrMo alloy sample: a) magnification X5000, scale 20 μm and b) magnification X1400 scale 50 μm

The microstructure of sample P1-NiCrMo is well highlighted by the SEM image in Fig. 5, which shows a microstructure in well-defined cells of compounds aligned in orthogonal rows between them. The P1-NiCrMo sample is made of a Ni-based alloy (≈ 70% by weight) with a content of Cr (20% by weight) and Mo (≈ 10% by weight). EDS investigations show that the sample is chemically homogeneous, the EDS spectrum in Fig. 6 shows all the spectral lines specific to the NiCrMo alloy. Also, the Ni line as well as that of Mo and Cr are well defined and are uniformly distributed in the investigated area.

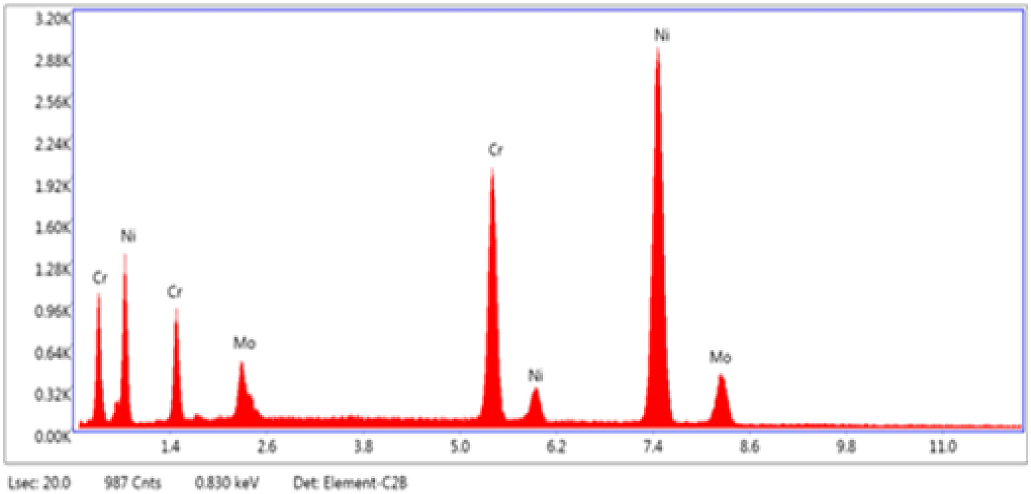
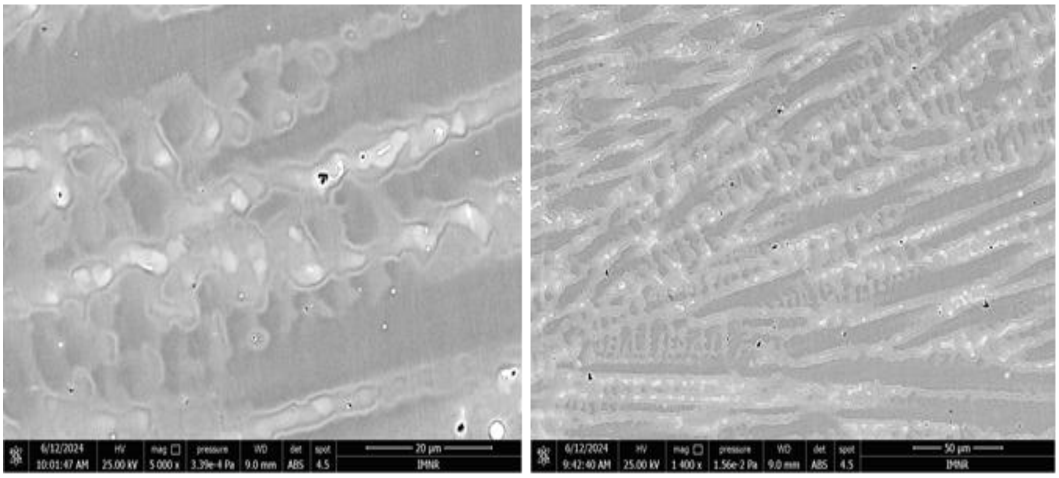


Fig. 6. EDS spectrum for P1-NiCrMo alloy sample



(a) **(b)**

Fig. 7. SEM image of the P2-NiCrMoTa alloy sample: a) magnification X5000, scale 20 µm and b) magnification X1400 scale 50 µm

Sample P2-NiCrMoTa is also well highlighted by the SEM image in Fig. 7, which shows a well-defined microstructure of compounds aligned in orthogonal rows to each other and are uniformly distributed in the investigated area. The P2-NiCrMoTa sample is made of an alloy based on Ni (≈ 65% by weight) with a content of Cr (20% by weight) and Mo (≈ 10% by weight) with the addition of Ta (≈ 5%).

EDS investigations show that the sample is chemically homogeneous, the EDS spectrum shown in Fig. 8 shows all the spectral lines specific to the NiCrMoTa alloy.

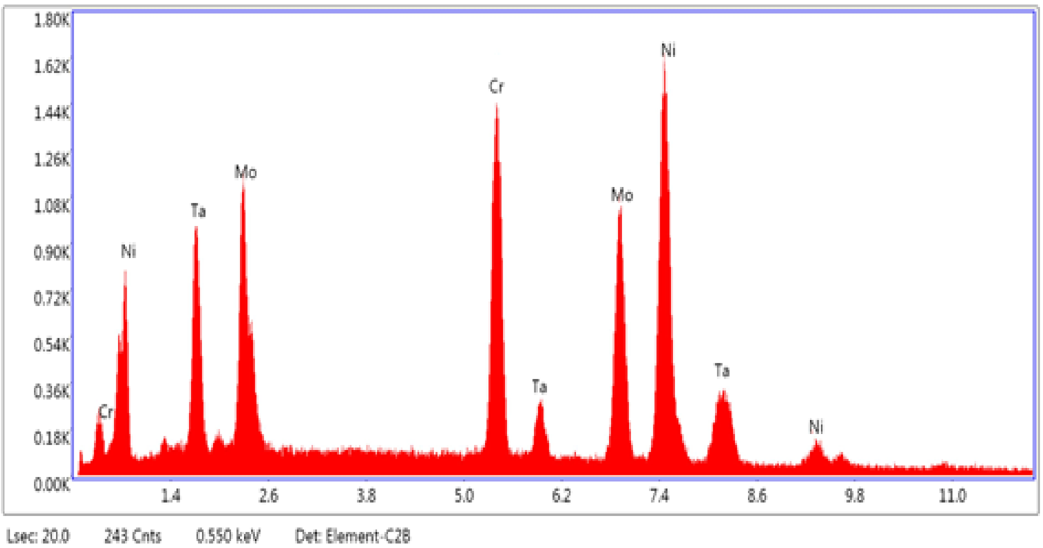


Fig. 8. EDS spectrum for P2-NiCrMoTa

Also, the Ni line as well as that of Mo, Cr and Ta are well defined and are uniformly distributed in the investigated area.

4. Conclusions

The development of biocompatible alloys by modifying the NiCrMo alloy represents a significant advance in the field of medical materials. Modifications of the NiCrMo alloy composition by additions of tantalum offer promising perspectives for the development of biocompatible medical alloys with improved mechanical and chemical properties. The evaluation of the physicochemical properties, using advanced analysis methods such as Scanning Electron Microscopy (SEM) and X-Ray Fluorescence Spectrometry (XRFS) revealed a uniform and homogeneous microstructural structure. These results suggest that the new alloy has a stable composition with a balanced distribution of elements, which is essential for its performance in biological environments. Also, the metallographic study on NiCrMo and NiCrMoTa samples highlighted a well-defined microstructure of compounds aligned in rows orthogonal to each other and uniformly distributed. This research can significantly contribute to the realization of more effective and safer implants, with a positive impact on the treatment of patients. Continued studies of these alloys will enable optimization of compositions and manufacturing processes, maximizing benefits for medical uses.

R E F E R E N C E S

[1] *M. Niinomi*, 4 - Co–Cr-based alloys, Editor(s): Cuie Wen, In: Woodhead Publishing Series in Biomaterials, Structural Biomaterials, Woodhead Publishing, 2021.

[2] *K.R. Yang, T. Hanawa, T.Y. Kwon, B.K. Min, M.H. Hong*, "Mechanical Property Comparison of Ni–Cr–Mo Alloys Fabricated via One Conventional and Two New Digital Manufacturing Techniques", Appl. Sci., 2021, Vol. **11**, Iss. 19, 9308.

[3] M. *Prem Kumar, M. Manikandan*, "Investigation of corrosion behaviour on Ni–Cr–Co and Ni–Cr–Mo alloys exposed to molten salt for thermal energy storage applications Corrosion Engineering, Science and Technology", The International Journal of Corrosion Processes and Corrosion Control, Vol. **58**, Iss. 1, 2022, pp. 49-60.

[4] *M.G. Jo, S.H. Ryu, K.I. Kim, D.E. Kim, J.I. Kim, K.T. Kim, S.S. Kim, G.S. Cho*, "A Study on the Microstructures and Mechanical Properties of Ni-Cr-Mo-V Low Alloy Steels", J. Korean Inst. Met. Mater., Vol. **60**, Iss. 4, pp. 251-262.

[5] *M. Buzatu, V. Geantă, R. Ştefănoiu, M. Buţu, M.I. Petrescu, M. Buzatu, V.G. Ghica, F. Niculescu, G. Iacob*, "Influence of the Tungsten Content on the Elastic Modulus of New Ti-15Mo-W Alloys Intended for Medical Applications", JOM - The Journal of The Minerals, Metals & Materials Society (TMS), Vol. **71**, Iss. 7, 2019, pp. 2272-2279.

[6] *J. Qi, L. Ma, P. Gong, W.M. Rainforth*, "Investigation of the wear transition in CoCrMo alloys after heat treatment to produce an HCP structure", Wear, Vol. **518–519**, 2023, 204649.

[7] *M. Buzatu, M.I. Petrescu, V. Geantă, R. Ştefănoiu, M. Buzatu, M. Buţu, G. Iacob, F. Niculescu*, "Full factorial design for Ti-Mo-W beta alloys to correlate the modulus of elasticity with the material parameters Md, Bo and e/a", U.P.B. Sci. Bull., Series B, Vol. **84**, Iss. 4, 2022, pp. 181-190.

[8] *S.S. Gvk*, "Co-Cr-Ni-Mo wires for medical applications: processing, mechanical, microstructure and fatigue characterization", Doctoral thesis, Nanyang Technological University, Singapore, 2019.

[9] *A. Haider, S.H.I. Jaffery, A.N. Khan, N. Qadir, X. Jing*, "Effect of cerium on mechanical, metallurgical and biomedical properties of NiCrMoB dental alloy", J. Mater. Res. Technol., Vol. **24**, 2023, pp. 5082-5093.

[10] *G. Mohandas, N. Oskolkov, M. McMahon, P. Walczak, M. Janowski*, "Porous tantalum and tantalum oxide nanoparticles for regenerative medicine", Acta Neurobiol Exp (Wars), Vol. **74**, Iss. 2, 2014, pp. 188-196.

[11] *H. Li, Z. Yao, J. Zhang, X. Cai, L. Li, G. Liu, J. Liu, L. Cui, J. Huang*, "The progress on physicochemical properties and biocompatibility of tantalum-based metal bone implants", Discover Applied Sciences, Vol. **2**, 2020, 671.

[12] *D. Cristea, I. Ghiuta D. Munteanu*, "Tantalum Based Materials for Implants and Prostheses Applications", Bulletin of the Transilvania University of Brasov. Series I: Engineering Sciences, Vol. **8(57)**, Iss. 2, 2015, pp. 151-158.

[13] *P. Aimone; K. Moser*, "Working with Tantalum and Tantalum Alloys", CORROSION 2003, San Diego, California, March 2003.

[14] *A. Turlybekuly, S.V. Plotnikov, A.A. Tsoraev, Y.G. Rusin, V.N. Angilevko, E.V. Krygin, M.V. Semenets, N.K. Erdybaeva, G.K. Uazyrkhanova, R.N. Kimosov, S.A. Zhanysov, A.A. Myakinin*, "Preparation of a ternary alloy of the Ti-Nb-Ta system for further use in medicine", Bulletin of the Karaganda University Physics Series, Vol. **90**, Iss. 2, 2018, pp. 56-62.

[15] *G. Maccauro, P.R. Iommetti, F. Muratori, L. Raffaelli, P.F. Manicone, C. Fabbriciani*, "An overview about biomedical applications of micron and nano size tantalum", Recent Pat Biotechnol., Vol. **3**, Iss. 3, 2009, pp. 157-165.