Obrabotka metallov (tekhnologiya, oborudovanie, instrumenty) = Metal Working and Material Science. 2022 vol. 24 no. 3 pp. 66–75
ISSN: 1994-6309 (print) / 2541-819X (online)
DOI: 10.17212/1994-6309-2022-24.3-66-75

NSTU NETI

Obrabotka metallov - Metal Working and Material Science

Journal homepage: http://journals.nstu.ru/obrabotka_metallov

Deformability of TiNiHf shape memory alloy under rolling with pulsed current

Vladimir Stolyarov [1, a, *], *Vladimir Andreev* [2, b], *Roman Karelin* [2, 3, c], *Umar Ugurchiev* [1, d], *Vladimir Cherkasov* [3, e], *Victor Komarov* [2, 3, f], *Vladimir Yusupov* [2, g]

[1] Mechanical Engineering Research Institute of RAS, 4 M. Kharitonyevskiy Pereulok, Moscow, 101990, Russian Federation
[2] Baikov Institute of Metallurgy and Materials Science, 49 Leninskiy Prospekt, Moscow, 119334, Russian Federation
[3] National University of Science and Technology MISIS, 4/1 Leninskiy Prospekt, 119049, Russian Federation

[a] https://orcid.org/0000-0001-7604-3961, vlstol@mail.ru, [b] https://orcid.org/0000-0003-3937-1952, andreev.icmateks@gmail.com,
[c] https://orcid.org/0000-0002-4795-8668, rdkarelin@gmail.com, [d] https://orcid.org/0000-0003-2072-6354, umar77@bk.ru,
[e] https://orcid.org/0000-0002-5450-3565, v.basenchikov@yandex.ru, [f] https://orcid.org/0000-0003-4710-3739, vickomarov@gmail.com,
[g] https://orcid.org/0000-0002-0640-2217, vsyusupov@mail.ru

ARTICLE INFO

Article history:
Received: 27 April 2022
Revised: 06 May 2022
Accepted: 18 June 2022
Available online: 15 September 2022

Keywords:
Shape memory alloys
Rolling
Pulse current
Structure
Deformability
Hardness

Funding
The study was carried out within the framework of the state task of IMET RAS No. 075-00715-22-00.

ABSTRACT

Introduction. The deformation capacity of materials is one of the main mechanical characteristics that determine the possibility of its production using various technological processes for metal forming. Among intermetallic compounds, a special role belongs to alloys with a high-temperature shape memory effect (*SME*) based on *TiNi* with the addition hafnium. Most of these alloys are not only difficult to deform, but also quite brittle. Therefore, the development of any technological schemes to increase the deformation capacity of these alloys is relevant. **The purpose of the work**: to study the deformation capacity and the possibility of using electric pulsed current during cold rolling of the *TiNiHf* alloy. This processing method has not previously been applied to these alloys. **In this work,** the deformation capacity during cold rolling of a strip 2 mm thick made of a hard-to-deform high-temperature *TiNi*-based shape memory alloy with the addition of hafnium is studied. To increase the deformability, an external action in the form of a high-density pulsed current of more than 200 A/mm^2 is investigated. **The research methods are**: X-ray analysis to assess the initial phase state; analysis of the evolution of true and engineering deformation to failure (appearance of visible macrocracks in the deformation zone); optical microscopy with magnification from 50 to 100 and measurement of *Vickers* hardness at room temperature. **Results and discussion**. An increase in the deformability under the influence of a pulsed current compared to rolling without current and the achievement of a maximum strain of 1.7 (true) and 85% (engineering) are established. The initial coarse-grained equiaxed martensitic microstructure (50 μm) is transformed into a microstructure elongated along the rolling direction, while the hardness increases by 50%. The absence of noticeable structural changes and the observed hardening may indicate a nonthermal effect of the current in increasing the deformability. Thus, the results of the conducted studies indicate the prospects of the method of rolling with a current of a hard-to-deform *TiNiHf* shape memory alloy as a method of metal forming.

For citation: Stolyarov V.V., Andreev V.A., Karelin R.D., Ugurchiev U.Kh., Cherkasov V.V., Komarov V.S., Yusupov V.S. Deformability of TiNiHf shape memory alloy under rolling with pulsed current. *Obrabotka metallov (tekhnologiya, oborudovanie, instrumenty) = Metal Working and Material Science*, 2022, vol. 24, no. 3, pp. 66–75. DOI: 10.17212/1994-6309-2022-24.3-66-75. (In Russian).

Introduction

The deformability is one of the mechanical characteristics that determines the ability of solid materials to change its shape and size under the influence of external factors, including forming processes. This characteristic affects the operational behavior of the deformed material and is especially relevant for the development of production technologies associated with rolling, pressing, drawing, upsetting. For various

*** Corresponding author**
Stolyarov Vladimir V., D.Sc. (Engineering), Professor
Mechanical Engineering Research Institute of RAS,
4 M. Kharitonyevskiy Pereulok,
101990, Moscow, Russian Federation
Tel.: 8 (915) 294-69-41, **e-mail:** vlstol@mail.ru

metallic materials deformability can be equal from a tenth to tens of percent, limiting or expanding the possibility of application of metal forming processes. The deformability of metallic materials before forming processes is commonly increased by application of thermal treatment (heating). However, in some cases heating is unacceptable due to accompanied changes in other properties (corrosion resistance, hydrogen embrittlement, etc.) or a decrease in economic efficiency. Deformation processes with the use of a pulsed electric current allows solving these problems for a number of brittle or hard-to-deform metals, steels and alloys based on *Ti*, *Zr*, *Al*, *Mg*, *Fe* [1-15]. Among the studied materials, a special role belongs to alloys based on the *TiNi* ordered intermetallic compound, which performs a shape memory (*SME*) and superelasticity effects at temperatures close to room temperature [16, 17]. Previous studies have revealed the prospect of forming process with a pulsed current for production of thin long-length semi-finished products from binary *Ti-Ni* shape memory alloys (*SMA*) [2, 3, 9]. *Ti-Ni SMA* are actively used in various sectors of the economy due to its unique properties. The finishing temperature of the reverse martensitic transformation in titanium nickelide of equiatomic composition is about 80-90 °C, which put bounds to its use at higher temperatures. Recently, high-temperature multicomponent alloys with a noticeably higher temperature of martensitic transformation, in which some of the nickel or titanium atoms are replaced by hafnium atoms, was also studied [18-24]. As compared to titanium nickelide, hafnium-doped alloys are not only difficult to deform, but rather brittle. The need for the practical use of these alloys in the form of long thin-section products imposes increased requirements on its deformability during rolling or drawing, especially at the final stages of manufacturing. Until now, there has been no information in the literature on the application of the electrostimulated forming process to *TiNi*-based ternary alloys with the addition of hafnium. Therefore, the development of any technologies, including electroplastic rolling, to increase the deformability of these alloys is relevant.

The purpose of the paper is to study the deformability and the possibility of application of pulsed current during cold rolling of the *TiNiHf* alloy. This treatment has shown its efficiency for titanium nickelide [3], however, it has not been previously applied to brittle hafnium-doped alloys, where the embrittling phase plays a significant role.

Materials and research methods

In the present study the *TiNiHf* alloy, obtained in the industrial center MATEK-SMA by the method of electron beam melting from charge materials: *TiNi* near stoichiometric alloy in the form of a rod with a diameter of 12 mm and a hafnium wire with a diameter of 1 mm, was used. The chemical composition of the ingot is given in Table 1. Samples for rolling were cut from the ingot by the method of electrical discharge cutting in the form of strips with dimensions of 2.0×6.0×131 mm^3.

The shape and dimensions of the ingot and the sample for rolling are shown in Fig. 1.

For flat rolling, a two-roll mill with a roll diameter of 65 mm was used. The pulse current was supplied from a generator with the following parameters: current J = 500–5,000 A, pulse duration $\tau \leq 1000$ µs and frequency in the range ν = 1–1000 Hz. The scheme of current supply and the direction of deformation is shown in Fig. 2.

The rolling rate and thickness reduction were 60 mm/s and 25 µm, respectively. The process was carried out at room temperature. To avoid overheating, the samples were cooled in water after each rolling pass. The uniform distribution of deformation along the length and thickness was ensured by rotating the sample around the longitudinal axis by 180° and changing the direction of rolling to the opposite.

Table 1

Chemical composition of the alloy

mass.%			at.%		
Ti	*Ni*	*Hf*	*Ti*	*Ni*	*Hf*
38.2	47.0	14.8	47.4	47.6	5.0

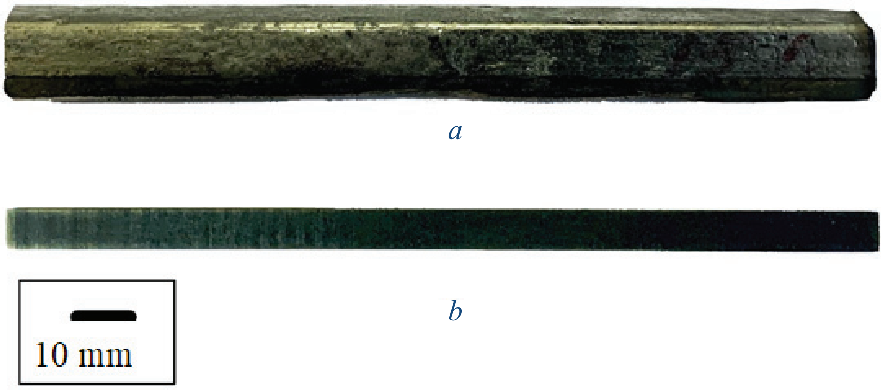

Fig. 1. Shape and dimensions of *TiNiHf* alloy samples:
a – ingot; *b* – strip for rolling

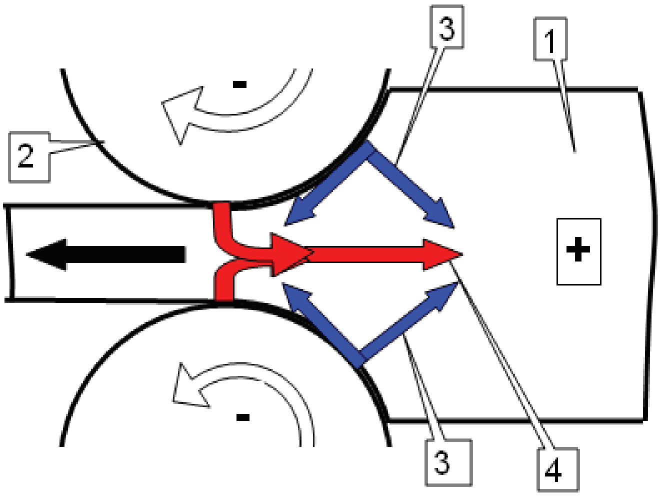

Fig. 2. Scheme of current supply and strain direction:
1 – work materials; *2* – cylindrical rolls; *3* – force direction;
4 – current direction

The current density *j* varied from 200 A/mm^2 at the beginning of the process to 580 A/mm^2 at the final passes with a pulse duration of 200 µs and a frequency of 500 Hz. At smaller values of current density, the deformation behavior of the alloy did not differ from that during rolling without current, and fracture occurred already after the first passes. The true strain *e* was calculated by the equation $e = ln\ S_0 / S_f$ (where S_0, S_f are the cross-sectional area of the strip before and after rolling).

The microstructure was studied using a *Versamet-2 Union* optical microscope with a magnification of 50 to 100. Samples for light microscopy were ground on abrasive paper with a grain size of P120 to P2,500, followed by polishing. After mechanical grinding and polishing, the samples were etched in following solutions: $1HF{:}3HNO_3{:}6H_2O_2$. The deformation hardening of the alloy was determined via *Vickers* hardness tests. The tests were carried out at room temperature on a *LECOM 400-A* hardness tester under a load of 1 N with an exposure of the indenter for 10 s.

Results and discussion

In the present paper a method for processing hard-to-deform brittle *TiNiHf* alloys with a reduced *Ni* content by cold rolling with a pulsed current was applied and studied for the first time.

Phase Composition and Microstructure

The X-ray diffraction pattern of the alloy in the initial state at room temperature is shown in Fig. 3. The lines of martensite and $(Ti, Hf)_2\ Ni$ phase are confidently indicated on the X-ray diffraction pattern. The absence of visible lines of the high-temperature phase – austenite – confirms that the temperature of the beginning of the reverse martensitic transformation exceeds 25 °C. A weak broadening of the X-ray lines indicates a low crystal lattice deficiency, which is typical for of a recrystallized structure. Thus, based on the results of X-ray phase analysis, it can be concluded that the embrittling $(Ti, Hf)_2\ Ni$ phase is contained in a significant amount in the initial sample.

The microstructure of the *TiNiHf* alloy in the initial state and after rolling with a current up to a strip with a thickness of 0.6 mm is shown in Fig. 4. In the initial state, *TiNiHf* alloy has a recrystallized structure

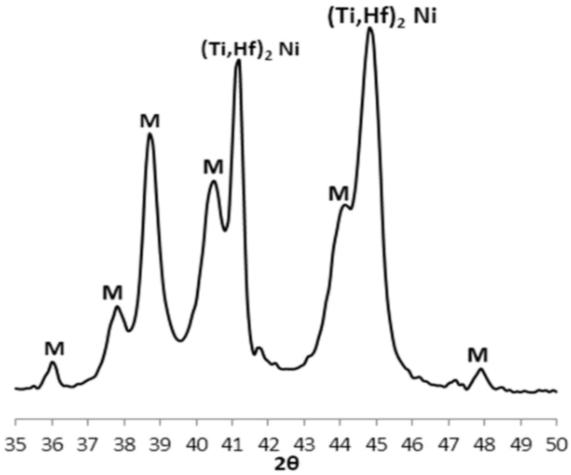

Fig. 3. X-ray diffraction pattern of the alloy in the initial state

with an average grain size in the longitudinal and cross-section directions of about 50 μm (Fig. 3, *a*, *b*). Thin bands of the martensite located inside the grains are observed. The presence of residual austenite is not excluded. The clusters of (*Ti*, *Hf*)$_2$ *Ni* type particles of the excess phase, formed immediately after melting, are observed at the grain boundaries [10]. It is assumed that the phase composition of the alloy at room temperature consists of a mixture of martensite, a small amount of residual austenite and the (*Ti*, *Hf*)$_2$ *Ni* phase with a volume fraction of about 20–25 %, estimated visually. The platelet shape of the intragranular phase and the results of the XRD study (Fig. 3) confirm this suggestion. Rolling with current leads to a change in the morphology of the grain structure: it becomes more elongated (Fig. 4, *c*). At the same time, an even more pronounced grain elongation in the transverse direction is observed (Fig. 4d), which may be explained by both the geometry of the sample and the features of the plastic flow of the alloy during rolling with current. This leads to a redistribution of particles of the (*Ti*, *Hf*)$_2$ *Ni* phase, which line up along the elongated boundaries of structural elements formed during rolling with current. It should be noted that, despite the large number of macrocracks on the side edges of the strip after rolling, intergranular and intragranular microcracks were not found at all stages of deformation.

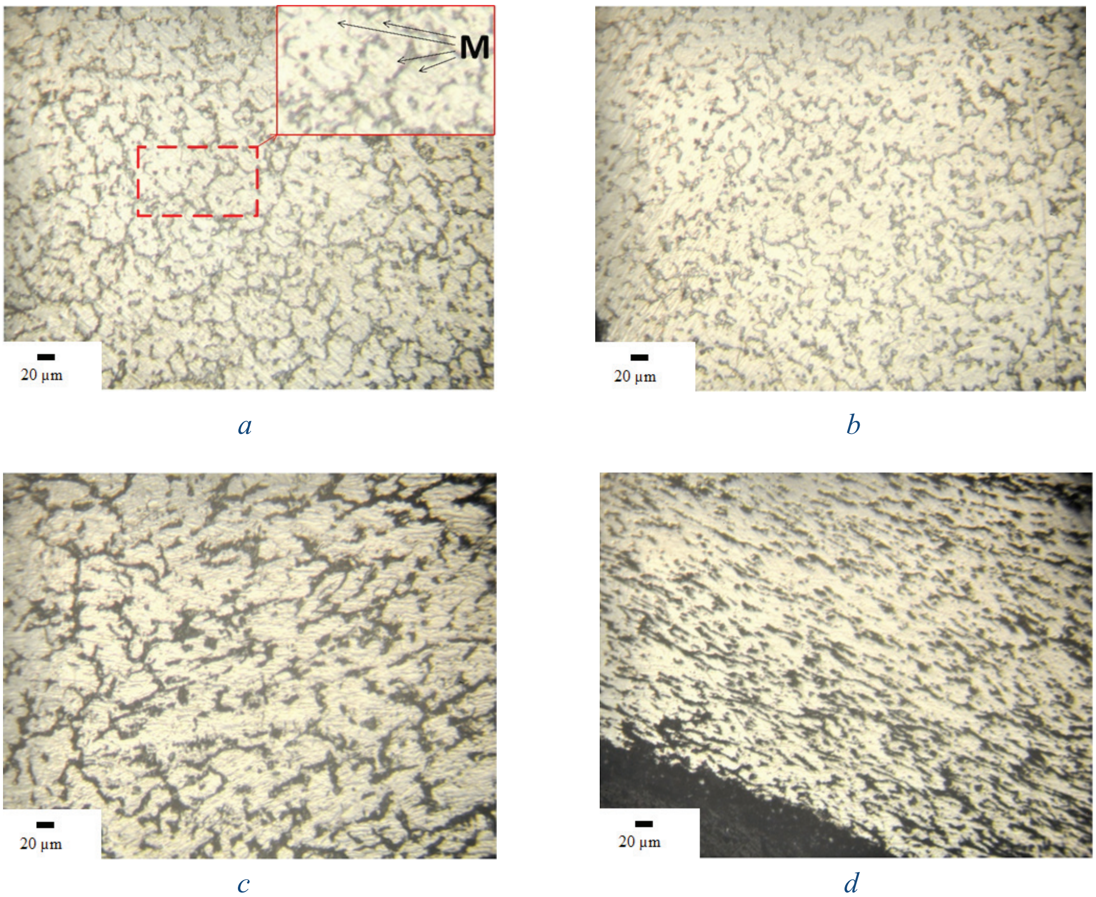

Fig. 4. Microstructure of the alloy in the initial (*a*, *b*) and current-rolled (*c*, *d*) states:
a, *c* – along the rolling direction; *b*, *d* – across the rolling direction

Deformability and Hardness

Experimental results have revealed that after rolling of flat samples without current (Fig. 5, *a*) or with current density $j < 200$ A/mm^2 (Fig. 3b), the *TiNiHf* alloy fractures brittle already after the first 3-4 passes ($e \leq 0.07$) and without the formation of edge defects (Fig. 5 *a*, *b*). In most cases, the sample is divided into several parts. It should be noted that the thickness reduction does not exceed 5 %.

The deformability increases with the increase of the current density $j \geq 200$ A/mm^2 allowing to preserve the entity of the sample (Fig. 5, *c*, *d*, *e*). The microfracture always starts from the side edges of the sample, which increases but does not lead to macrofracture (Fig. 6). The edge microcracks formed during the rolling process due to the concentration of predominantly tensile stresses during the transition from the bulk state in the original sample to the plane-stressed state in a thin sample. Obviously, the application of a pulsed current during the rolling process inhibits the formation and propagation of cracks.

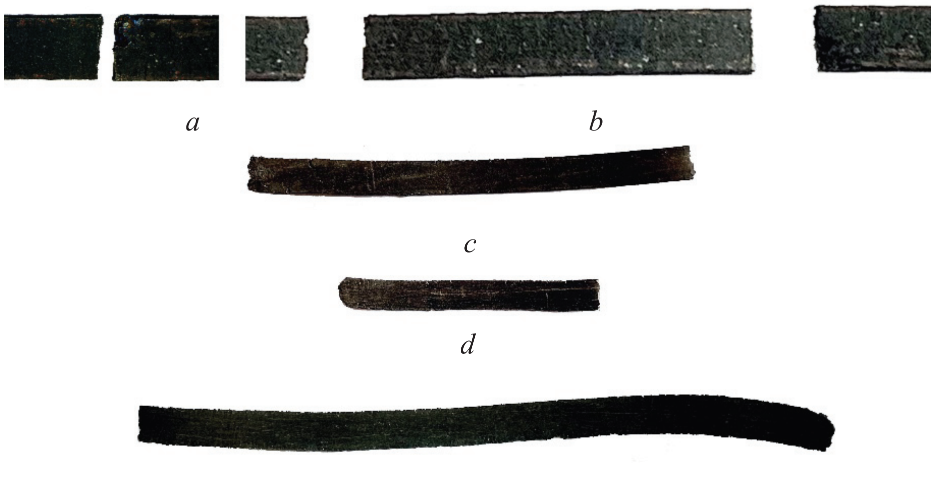

Fig. 5. Appearance of samples during rolling without current (*a*) and with current (*b*, *c*, *d*, *e*) at true deformation:
a–e = 0; *b*–e =0.07; *c*–e = 0.39; *d*–e = 0.85; *f*–e = 1.47

The change in the dimensions of the sample cross section, as well as the hardness value, engineering and true strain during the rolling process of the sample with a pulsed current are presented in Table 2.

Fig. 6. Stereomicroscopic image of the sample rolled with current, j = 580 A/mm^2, e = 1.47

The obtained results and analysis of the hardness value after rolling showed that an increase in the accumulated strain after rolling with current leads to almost linearly increase in the hardness value (Table 2). It can be assumed that the strengthening is a consequence of several factors: an increase in the volume fraction of martensite due to the transformation of residual austenite during deformation; changes in the starting temperature of the forward martensitic transformation M_s as compared to the measurement temperature (20 °C); an increase in the dislocation density and substructural refinement and an increase in the number of intermetallic particles at the grain boundaries. The nature of deformation hardening and the absence of the signs of recrystallization also indicate the minimum thermal effects in the process of rolling with current.

Table 2

Dimensions of the strip section, deformation and hardness during rolling with current

Pass No.	Initial section, mm	Final section, mm	Engineering deformation ratio, %	True deformation, *e*	*HV*
Without rolling	2.0 × 6.0	2.0 × 6.0	0	0	310
1–36	2.0 × 6.0	1.15 × 7.1	42.5	0.39	340
37–60	1.15 × 7.1	0.62 × 8.3	69.0	0.85	385
60–84	0.62 × 8.3	0.30 × 9.2	85.0	1.47	490

Conclusions

1. Flat rolling of the *TiNiHf SMA* strip with a thickness of 2 mm at room temperature under a pulse current with the density of more than 200 A/mm^2 allows accumulating the maximum value of true strain $e = 1.47$ without bulk destruction.

2. The absence of noticeable structural-phase changes and the observed deformation hardening indicate a non-thermal effect of the current in the significant increase of the deformability.

References

1. Troitskii O.A., Baranov Yu.V., Avramov Yu.S., Shlyapin A.D. *Fizicheskie osnovy i tekhnologii obrabotki sovremennykh materialov (teoriya, tekhnologiya, struktura i svoistva)*. V 2 t. T. 1 [Physical foundations and technologies for processing modern materials (theory, technology, structure and properties). In 2 vols. Vol. 1]. Izhevsk, Instite of Computer Technologies Publ., 2004. 590 p.

2. Gurtovaya I.B., Inaekyan K. E., Korotitskii A.V., Ugurchiev U.Kh., Makushev S.Yu., Khmelevskaya I.Yu., Danilova E.S., Sergeeva A.E., Stolyarov V.V., Prokoshkin S.D. Vliyanie rezhimov elektroplasticheskoi deformatsii na deformiruemost’ i funktsional’nye svoistva splava Ti-Ni s pamyat’yu formy [Influence of electroplastic deformation modes on deformability and functional properties of Ti-Ni shape memory alloy]. *Zhurnal funktsional’nykh materialov = Journal of functional materials*, 2008, vol. 2, no. 4, pp. 130–137.

3. Potapova A.A., Stolyarov V.V., Bondarev A.B., Andreev V.A. Issledovanie vozmozhnosti primeneniya elektroplasticheskoi prokatki dlya polucheniya prutkov iz splava TiNi [Investigation of the possibility of using electroplastic rolling to obtain bars from the TiNi alloy]. *Mashinostroenie i inzhenernoe obrazovanie = Mechanical Engineering and Engineering Education*, 2012, no. 2, pp. 33–38.

4. Medentsov V.E., Stolyarov V.V. Osobennosti deformirovaniya, struktura i mekhanicheskie svoistva splava VT6 pri elektroplasticheskoi prokatke [Peculiarities of deformation, structure and mechanical properties of VT6 alloy during electroplastic rolling]. *Deformatsiya i razrushenie materialov = Deformation and Fracture of Materials*, 2012, no. 12, pp. 37–41.

5. Brodova I.G., Shirinkina I.G., Astaf’ev V.V., Yablonskikh T.I., Potapova A.A., Stolyarov V.V. Effect of pulsed current on structure of Al–Mg–Si aluminum-based alloy during cold deformation. *Physics of Metals and Metallography*, 2013, vol. 114 (11), pp. 940–946. DOI: 10.1134/S0031918X13110021.

6. Ivanov A.M., Ugurchiev U.Kh., Stolyarov V.V., Petrova N.D., Platonov A.A. Kombinirovanie metodov intensivnoi plasticheskoi deformatsii konstruktsionnykh stalei [Combination of severe plastic deformation methods of structure steels]. *Izvestiya vysshikh uchebnykh zavedenii. Chernaya metallurgiya = Izvestiya. Ferrous Metallurgy*, 2012, no. 6, pp. 54–57.

7. Xu Z., Tang G., Tian S., Ding F., Tian H. Research of electroplastic rolling of AZ31 Mg alloy strip. *Journal of Materials Processing Technology*, 2007, vol. 182 (1–3), pp. 128–133. DOI: 10.1016/j.jmatprotec.2006.07.019.

8. Qian L., Zhan L., Zhou B., Zhang X., Liu S., Lv Z. Effects of electroplastic rolling on mechanical properties and microstructure of low-carbon martensitic steel. *Materials Science and Engineering: A*, 2021, vol. 812, p. 141144. DOI: 10.1016/j.msea.2021.141144.

9. Zhu R.F., Tang G.Y., Shi S.Q., Fu M.W. Effect of electroplastic rolling on the ductility and superelasticity of TiNi shape memory alloy. *Materials and Design*, 2013, vol. 44, pp. 606–611. DOI: 10.1016/j.matdes.2012.08.045.

10. Guan L., Tang G., Chu P.K. Recent advances and challenges in electroplastic manufacturing processing of metals. Journal of Materials Research, 2010, vol. 25 (7), pp. 1215–1224. DOI: 10.1557/JMR.2010.0170.

11. Zhu R., Tang G., Shi S., Fu M. Effect of electroplastic rolling on deformability and oxidation of NiTiNb shape memory alloy. *Journal of Materials Processing Technology*, 2013, vol. 213 (1), pp. 30–35. DOI: 10.1016/j.jmatprotec.2012.08.001.

12. Mal'tsev I.M. Electroplastic rolling of metals with a high-density current. *Russian Journal of Non-Ferrous Metals*, 2008, vol. 49, pp. 175–180. DOI: 10.3103/S1067821208030097.

13. Li X., Wang F., Li X., Tang G., Zhu J. Improvement of formability of Mg–3Al–1Zn alloy strip by electroplastic-differential speed rolling. *Materials Science and Engineering: A*, 2014, vol. 618, pp. 500–504. DOI: 10.1016/j.msea.2014.09.060.

14. Guo D.F., Deng W.K., Song P., Lv X.L., Shi Y., Qu Z.H., Zhang G.S. Effect of strain rate on microstructure and mechanical properties of electroplastic rolled ZrTi alloy. *Advanced Engineering Materials*, 2022, p. 202101366. DOI: 10.1002/adem.202101366.

15. Tiwari J., Pratheesh P., Bembalge O.B., Krishnaswamy H., Amirthalingam M., Panigrahi S.K. Microstructure dependent electroplastic effect in AA 6063 alloy and its nanocomposites. *Journal of Materials Research and Technology*, 2021, vol. 12, pp. 2185–2204. DOI: 10.1016/j.jmrt.2021.03.112.

16. Komarov V.S., Khmelevskaya I., Karelin R., Kawalla R., Korpala G., Prahl U., Prokoshkin S. Deformation behavior, structure, and properties of an aging Ti-Ni shape memory alloy after compression deformation in a wide temperature range. *JOM*, 2021, vol. 73 (2), pp. 620–629. DOI: 10.1007/s11837-020-04508-7.

17. Karelin R.D., Khmelevskaya I.Y., Komarov V.S., Andreev V.A., Perkas M.M., Yusupov V.S., Prokoshkin S.D. Effect of quasi-continuous equal-channel angular pressing on structure and properties of Ti-Ni shape memory alloys. *Journal of Materials Engineering and Performance*, 2021, vol. 30 (4), pp. 3096–3106. DOI: 10.1007/s11665-021-05625-3.

18. Babacan N., Bilal M., Hayrettin C., Liu J., Benafan O., Karaman I. Effects of cold and warm rolling on the shape memory response of Ni50Ti30Hf20 high-temperature shape memory alloy. *Acta Materialia*, 2018, vol. 157, pp. 228–244. DOI: 10.1016/j.actamat.2018.07.009.

19. Tong Y., Shuitcev A., Zheng Y. Recent development of TiNi-based shape memory alloys with high cycle stability and high transformation temperature. *Advanced Engineering Materials*, 2020, vol. 22 (4). DOI: 10.1002/adem.201900496.

20. Young A.W., Wheeler R.W., Ley N.A., Benafan O., Young M.L. Microstructural and thermomechanical comparison of Ni-rich and Ni-lean NiTi-20 at.% Hf high temperature shape memory alloy wires. *Shape Memory and Superelasticity*, 2019, vol. 5 (4), pp. 397–406. DOI: 10.1007/s40830-019-00255-0.

21. Belbasi M., Salehi M.T. Influence of chemical composition and melting process on hot rolling of NiTiHf shape memory alloy. *Journal of Materials Engineering and Performance*, 2014, vol. 23 (7), pp. 2368–2372. DOI: 10.1007/s11665-014-1006-8.

22. Javadi M.M., Belbasi M., Salehi M.T., Afshar M.R. Effect of aging on the microstructure and shape memory effect of a hot-rolled NiTiHf alloy. *Journal of Materials Engineering and Performance*, 2011, vol. 20 (4), pp. 618–622. DOI: 10.1007/s11665-011-9885-4.

23. Karaca H.E., Saghaian S.M., Ded G., Tobe H., Basaran B., Maier H.J., Noebe R.D., Chumlyakov Y.I. Effects of nanoprecipitation on the shape memory and material properties of an Ni-rich NiTiHf high temperature shape memory alloy. *Acta Materialia*, 2013, vol. 61 (19), pp. 7422–7431. DOI: 10.1016/j.actamat.2013.08.048.

24. Amin-Ahmadi B., Pauza J.G., Shamimi A., Duerig T.W., Noebe R.D., Stebner A.P. Coherency strains of H-phase precipitates and their influence on functional properties of nickel-titanium-hafnium shape memory alloys. *Scripta Materialia*, 2018, vol. 147, pp. 83–87. DOI: 10.1016/j.scriptamat.2018.01.005.

Conflicts of Interest

The authors declare no conflict of interest.