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CONTRIBUTION TO THE INVESTIGATION OF CORROSION PROPERTIES OF THE Ni-Ti ALLOY WITH SHAPE MEMORY

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Responsible application of metals with shape memory needs to know degradation processes taking place during their exploitation in real conditions. The contribution investigates corrosion properties of an Ni-Ti alloy containing 55.2 % Ni and 44.8 % Ti in physiological salt solution (0.9 % NaCl at 40 ± 1 °C). The performed laboratory tests found out a high corrosion resistance of the material used mainly in human medicine for implants. By measuring the electrochemical characteristics it could be acknowledged that this is related to the formation of a passive state on the alloy surface during its exploitation.

Key words: *metallic materials with shape memory, corrosion properties*

Doprinos istraživanju korozivnih svojstava slitine Ni-Ti s pamćenjem oblika. Odgovorna primjena metala s pamćenjem oblika mora poznavati procese degradacije koji se dešavaju tokom eksploatacija u realnim uvjetima. Doprinos istražuje svojstava korozije slitine Ni-Ti koja sadrži 55.2 % Ni i 44.8 % Ti u fiziološkoj otopini soli (0.9 % NaCl pri 40 ± 1 °C). Provedenim laboratorijskim ispitivanjima utvrđena je visoka otpornost na oksidaciju materijala koji se u humanoj medicini koriste pretežito za implantaciju. Mjerenjem elektrokemijskih osobina moglo se potvrditi da se to odnosi na formiranje pasivnog stanja na površini slitine tijekom njene eksploatacije.

Ključne riječi: *metalni materijali s pamćenjem oblika, svojstva korozije*

INTRODUCTION

Metallic materials with shape memory are functionally active materials with a phenomenon of thermoplastic martensitic transformation. After an appropriate thermal treatment a relatively soft, deformable martensite is forming in them. In this structure state the material can be formed to a desired shape by cold deformation. The back to the original state can be achieved by heating up, via transformation of the deformed martensite.

The shape memory phenomena are present in several metallic materials, but the Cu and Ni-Ti based materials have the greatest practical importance. They are used in regulation and automation technique and as implants in human medicine, mainly. Reliable exploitation of these materials is conditioned by understanding the degradation processes taking place during their exploitation in real conditions.

A good corrosion resistance is one of the limiting factors for their application. In the contribution some results of laboratory tests of corrosion properties of the Ni-Ti alloy in 0.9 % NaCl solution at 40 ± 1 °C [1] are summarized.

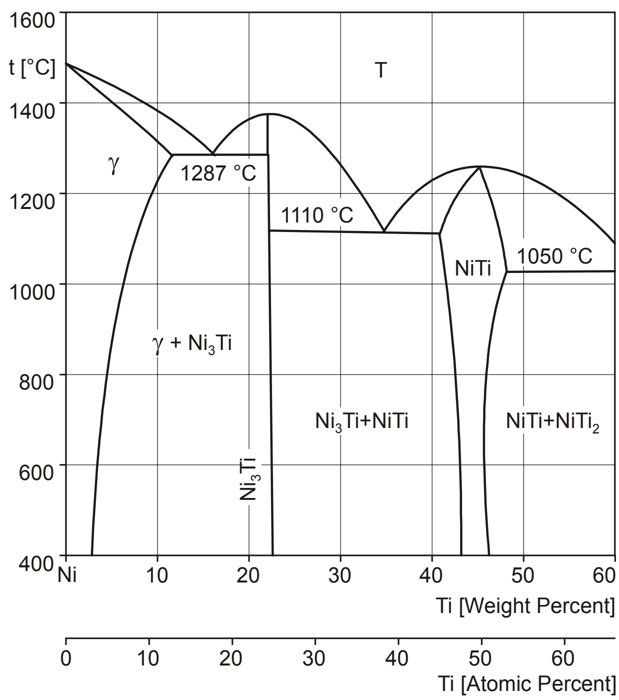

Figure 1. **Binary diagram of Ni-Ti**
Slika 1. **Binarni dijagram Ni - Ti**

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EXPERIMENTAL

The tested material with a composition of 44.8 wt. % of Ti and 55.2 wt. % of Ni was prepared under laboratory conditions. The process of preparing consisted of refining of the raw materials in a vacuum and a plasma arc furnaces, from melting and casting in an induction furnace, followed by homogenization annealing at 950 °C/2h, warm rolling and cold forming with an intermediate annealing at 700 °C/10 min. [2].

From the binary diagram of Ni-Ti in Figure 1. it can be followed that at the given chemical composition the alloy is formed by titanium nickelide - NiTi, or in case also by $NiTi_2$ and Ni_3Ti, respectively [3]. The appearance of the microstructure of tested samples is in Figure 2..

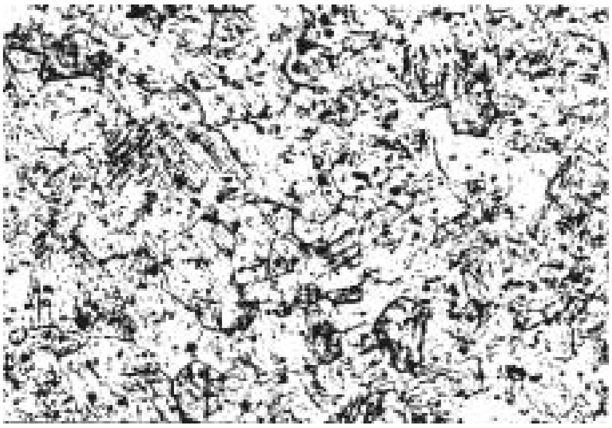

Figure 2. **Microstructure of Ni-Ti alloy, 250x, electrolyt. etching**
Slika 2. **Mikrostruktura slitine Ni-Ti, uvećana 20 x, elektrolitno nagrizanje**

Also the starting components were tested, namely titanium iodide and nickel of electrolytic purity, for the purpose of comparison. The surface of all samples was ground and mechanically polished prior to testing. In respect to the predominant application of this alloy for implants in human medicine, the corrosion tests were performed in the physiological salt solution of 0.9 % NaCl at the temperature of 40±1 °C. Several testing methods were applied to achieve complex evaluation of the corrosion properties. These were: gravimetric analysis, measuring the corrosion potentials towards a saturated calomel electrode, measuring the potentiodynamical polarization curves and the polarization resistance [1].

The weight losses after 300 days of testing in 0.9 % NaCl solution are in Figure 3.. These were calculated from the results of gravimetric analysis, the accuracy of sample weighing was ± 0.00005 g. The results of this analysis for NiTi are between the results established for Ni and Ti, and they are placed closer to the Ti results. The corrosion rates of Ni and Ti, established by the test, are in concordance with the results published in [4]. The corrosion rate of NiTi

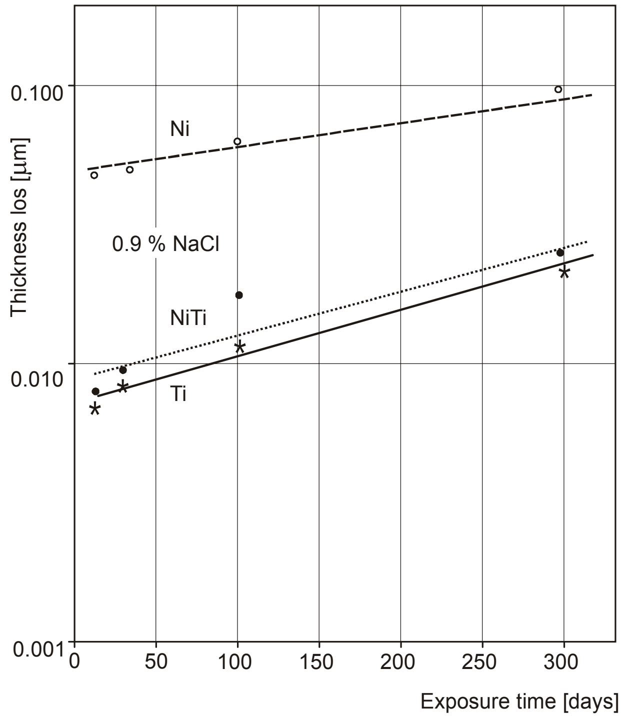

Figure 3. **Weight loss kinetics during the immersing test**
Slika 3. **Ispitivanje kinetičkog gubitka energije uranjanjem**

samples is decreasing with the prolongation of testing time, Figure 4.. In this figure the corrosion rates are compared

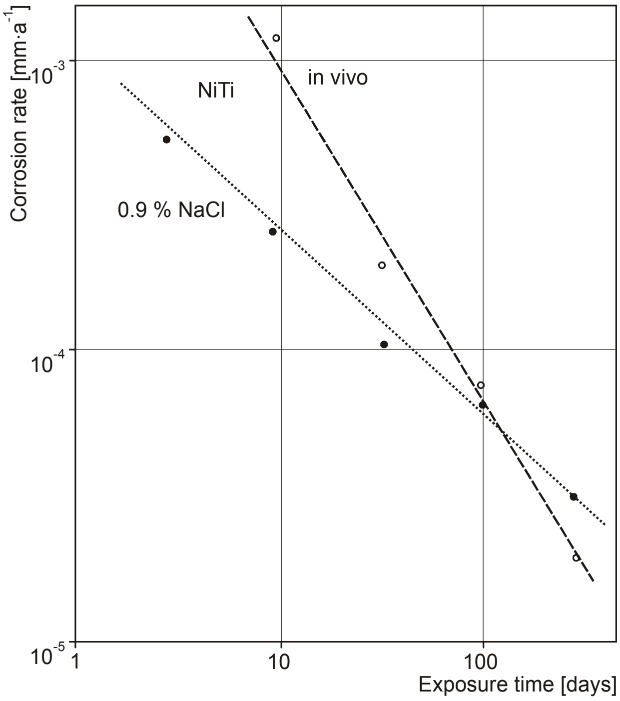

Figure 4. **Corrosion rate changes of samples with the exposure time in our test**
Slika 4. **Promjena na uzorcima ovisno o stupu korozije i vremenu izloženosti njenom djelovanju**

with the results published in [5] for NiTi samples implanted into a living organism (in vivo). From this comparison it can be followed that at the beginning of the exposition the "in vivo" corrosion prevails, but with advancing the exposition time both rates are becoming to be equal, and later the corrosion of Ni-Ti alloy in the living organism becomes slower. It is in concordance with the results published in [6], according to which after a longer exposure time the corrosion rate of implants in the organism is up to one order lower as the rate measured in the model test under laboratory conditions.

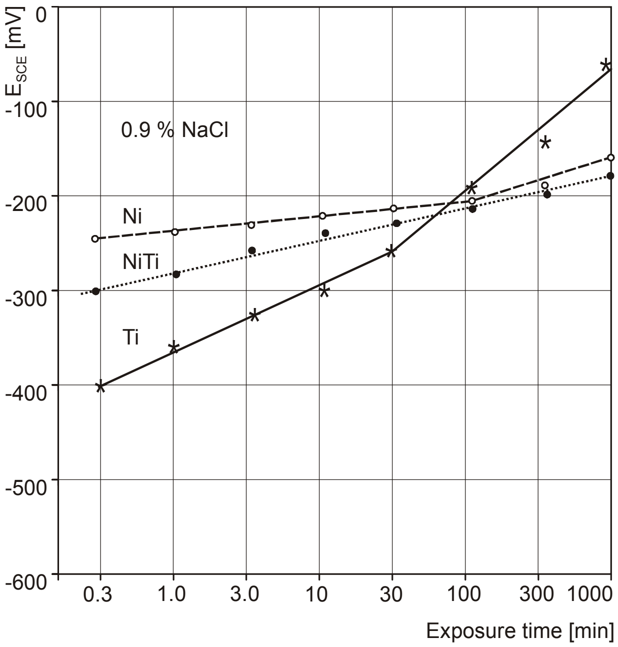

Figure 5. **Time dependencies of the electrode potential of samples**
Slika 5. **Ovisnost potencijala elektrode uzoraka o vremenu**

The time dependencies of the electrode potential of NiTi samples and of Ni and Ti basic components tested in 0.9 % NaCl can be found in Figure 5.. The values of Ti potential as a strong negative and that of Ni as a positive component are giving the possible ranges of these potentials in the tested NiTi specimens at the beginning of the test. The time shifts of the potentials for all samples are directed to the more positive values; this tendency is the strongest for Titanium, i.e., that Ti has the highest passivation ability in the applied electrolyte.

The basic electrochemical properties of the NiTi alloy and its starting components result from the potentio-dynamic polarisation curves in Figure 6.. The properties of Ni and Ti are very different. Nickel has an active state of corrosion in the anodic part of the curve, at the same time Titanium is passive. The Ni-Ti alloy is passivated like Ti, both have in the passive state similar values of current densities J. The measured values of the corrosion characteristics - the corrosion potential E_{kor}, the potential of breakthrough E_B and the passivating current density J_p are given in Table 1..

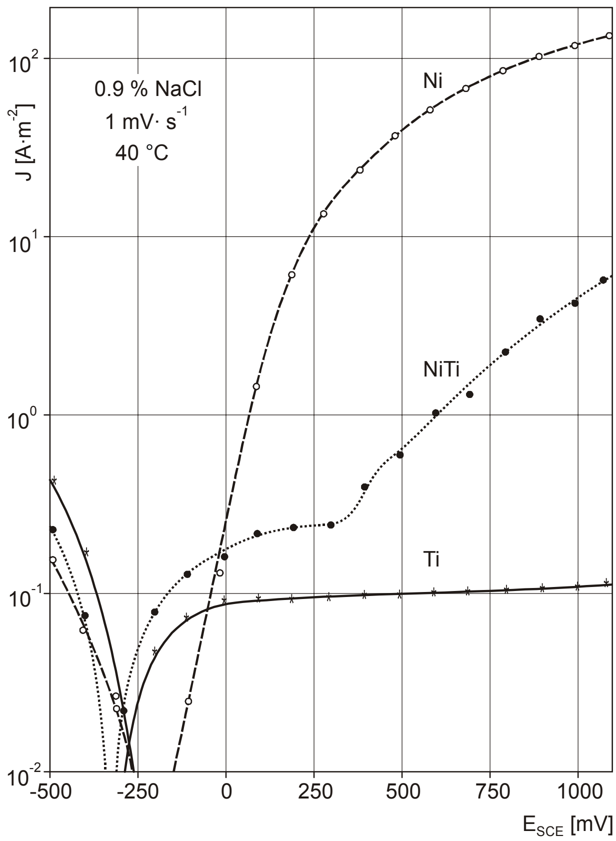

Figure 6 . **Potentio-dynamic polarization curves**
Slika 6. **Krivulja potencijalno dinamičke polarizacije**

Table 1. **The measured values of the corossion characteristics**
Tablica 1. **Izmjerene vrijednosti svojstava korozije**

Specimen	E_{kor} [mV]	E_B [mV]	E_B- E_{kor}[mV]	J_p [A·m^{-2}]
Ni	-156	-	-	-
NiTi	-325	345	670	0.28
Ti	-298	>5000	>5298	0.11

At reaching the breakthrough potential E_B a point damage of the passive layer is taking place. This is accompanied by an increase of the current density J. Corrosion properties of the NiTi alloy in chloride environment are thus bimodal, up to the potential +345 mV (E_B) they are close to the properties of Ti, in the region of more positive potentials they are approaching that of Nickel. The E_B potential, like other polarization characteristics, depends on the chloride concentration in the electrolyte, on the environment temperature [7], and on the further parameters of exposition. Because the shift of the corrosion potential with temperature is not marked very much, the difference of potentials E_B - E_{kor} is changing mostly because of the change of breakthrough potential which, with the increase of the temperature, is decreasing [6]. The value of $\Delta E_B = E_B - E_{kor}$ at $T = 40$ °C is 670 mV, which gives evidence of a good resistance of the Ni-Ti alloy against pitting corrosion in the solution of 0.9 % NaCl. This fact was confirmed also by the surface repassivation method [1], [8-9].

Polarization resistance R_p of the samples Ni, NiTi, and Ti was established by the method of two-electrode connection of samples described in [8]. It is considered that the amount of the immediate corrosion rate of the corroding material is inversely proportional to the immediate value of the polarization resistance. The values measured after 24 h long immersion in 0.9 % NaCl solution at 40 °C were: 0.12 $\Omega \cdot m^2$ for Ni, 0.39 $\Omega \cdot m^2$ for NiTi, and 0.58 $\Omega \cdot m^2$ for Ti. These results confirm the fact that the corrosion resistance of NiTi alloy is between the corrosion resistances of the both starting components, Ni and Ti.

CONCLUSIONS

From results of the corrosion resistance tests of titanium nickelid NiTi with the shape memory can be concluded that the material has a good corrosion resistance at conditions modeling the corrosion conditions of bioimplants.

The slow corrosion rate is connected with origination of a passive state on the exposed surface of NiTi, which is close to the passivity of Titanium. Susceptibility to pitting corrosion, which occurs in passivating metals in chloride environment, was not noticed under applied testing conditions as well. The determined value of $E_B - E_{kor} = 670$ mV at 40 °C gives evidence that at applied conditions the Ni-Ti alloy has a good resistance towards this specific form of corrosion.

REFERENCES

1. S. Tuleja: Corrosion of materials with shape memory. (in Slovak) [Closing Report of Task A3/4-4], Košice, 1990, HF TU
2. M. Proksa, et. all.: Constitution and Properties of Technically Utilizable Metalloids. (in Slovak) [Research Report], Bratislava, 1990, SjF SVŠT, KZZ and PM
3. B. A. Kolačev, et all.: Material science and thermal treatment of non-ferrous metals and alloys. (in Russian), Moskva, MISIS, 2001, 1st Ed
4. L. L. Migalj, T. A. Taricyna: Corrosion resistance of materials in halogenides and their solutions. (in Russian), Metallurgija, Moskva, 1988, 1st Ed.
5. M. D. Shibi Lu: Medical Applications of Ni-Ti Alloys in China. In: Engineering Aspects of Shape Memory Alloys, London, Butherworth-Hainemann, 1990, 3
6. M. Reevie, N. Greene: Journal Biomet. Mater. Research, 1969, 465
7. J. Kocich, et all.: Corrosion resistance of materials with shape memory. (in Slovak) In: Pokrokové materiály v konštrukčnej praxi (Proceedings of the Conference: Advanced Materials in Engineering Practice), Stará Lesná, 1993, 236
8. G. Bensmann, F. Baumgart: Technische Mitteilungen, Krupp Forschungsbericht, 49, 1982, 123
9. S. Tuleja: Corrosion and Protecting of Metals (in Slovak), (Seminar Instructions) Košice, 1984, HF VŠT