Prospects of Using Titanium Nickelide Implants with Modified Surface in Dental Implantology

V. V. Razdorsky

Translated from *Byulleten' Eksperimental'noi Biologii i Meditsiny*, Vol. 145, No. 6, pp. 707-713, June, 2008
Original article submitted October 31, 2007

Corrosion resistance and biocompatibility of 60 specimens of titanium nickelide with modified surfaces implanted into spongy bone were studied in rabbit experiments. Specimens modified by molybdenum ions exhibited high inertness and favorable tissue reaction. No accumulation of nickel and titanium ions in animal organs was detected.

Key Words: *implant surface modification; biocompatibility; inertness*

The majority of modern medical construction materials are not indifferent for human body. Metal objects lead to the appearance of galvanic currents causing a variety of disorders [1,3].

Corrosion of metal articles deteriorates the strength and plasticity of the material and its electrical and optical characteristics. Components of alloys (metal ions) accumulate in the adjacent tissues and distant organs [2,5].

Two methods for improving biocompatibility of metals are used in research and practical medicine. One of them, the search for and development of new alloys without physicochemical characteristics harmful for human body, is largely exhausted. The other is improvement of biocompatibility of materials most fit for implantation by modifying their surface. This method is becoming rather popular, as it is rather economic and allows the modification of the surface of a ready article [2,6].

As a result of modification, known materials acquire new useful characteristics, but regularities of their behavior in the body remain little studied.

Titanium nickelide alloy is new for medicine; its properties are unique: it is flexible and superelastic, possesses a thermomechanical shape memory; but it was not used in medicine as the implantation material for a long time.

Despite negative results of studies of toxic, carcinogenic, and mutagenic effects of titanium nickelide implants on the body and proven corrosion resistance in the organism, its safety is still doubted. The cause of negative attitude to titanium nickelide as an implantation material is its composition with equal shares of nickel and titanium [4,6].

The presence of barrier layers from combinations of elements tolerant of living tissues, such as zirconium and molybdenum, or modification by ionic and electron beams can limit and even completely block the presumable release of nickel into the environment and its accumulation in tissues.

We compared biocompatibility of titanium nickelide implants with surface modified by different methods *in vivo* in experiments on rabbits and discussed the prospects for their use as intermediate support for permanent bridge dentures.

MATERIALS AND METHODS

The study was carried out on 1-1.5-month-old rabbits (n=15; 280-350 g). The animals were purchased at a farm specialized in animal breeding for vivariums and pet shops. Individual certificates with vaccination and quarantine charts were provided for all animals. Anesthesia, observation of the

Novokuznetsk State Institute for Continuous Medical Education, Federal Agency for Health Care and Social Development. ***Address for correspondence:*** lotos200@mail.ru. V. V. Razdorsky

0007-4888/08/1456-0758

animals after surgery, and sacrifice (by electric shock) were carried out by qualified veterinarians.

The study was carried out on alloys smelted by electric arc 6-fold re-smelting from chemically pure components. For homogenization of the structure all components were annihilated in vacuum of at least 10^{-3} Pa during 1 h at 1073 K and cooled in the furnace. The surface layer was cleaned by mechanical grinding with subsequent electrolytic polishing.

Introduction of zirconium, molybdenum, and silver ions in surface layers of the implant was carried out at the mean accelerating voltage of 60 kV and pulse frequency of 50 Hz. Irradiation doses for all ions were ~1.5×10^{17} ion/cm^2.

Electron radiation treatment of the surface consisted in repeated (up to 50 pulses) irradiation of the sample surface by low-energy (up to 30 keV) strong current (up to 30 kA) electron beam in the surface smelting modes (2-3 μsec, 3-10 J/cm^2) under high vacuum conditions [2].

The implants used in the experiments were shaped as plates or disks 0.3 mm thick and linear size up to 10 mm. Optical metallography of the surface of all specimens was carried out on an Axiove 12T-200 high resolution optical microscope (Carl Zeiss).

Implantation was carried out as follows. After uncovering of the ileac bone crest, a hole was drilled to match the implant which was completely embedded in the hole. The specimens were distributed along the right crest at a distance of at least 5 mm: No. 4 (molybdenum ion modification), No. 1 (electroradiomodification), No. 2 (zirconium ion modification). On the left, specimens No. 5 from VT-8 allow and No. 3 (with surface modified by silver ions) were implanted.

The date of the operation and location of implants were recorded in the passport of the animal. The animals were sacrificed after 6.5 months, weighed, autopsied, and the organs were examined. The organs were weighed on analytical scales (0.001 precision) and dried on glass at 50°C in the drying chamber. Intact animals served as the control.

Metal elements in tissues and organs of experimental animals were analyzed by a Quant'X 600 X-ray fluorescent spectrometer. Quantitative element analysis in the biological samples was carried by the relationship between characteristic X-ray radiation and the element concentration using the calibration curves, which were plotted experimentally. Increase of the element concentration in experimental animals was expressed in percent of the normal values in control animals.

Both upper flaring portions of the ilium were mobilized, resected as a complex, and separated longitudinally using a circular saw. Macropreparations with the implants were examined and photographed. Bone blocks with the implants were isolated. The surface relief and element composition of the bone and implant capsule with the adjacent tissues were examined. The symmetrical bone block was plunged in 7% neutral formalin for histological study.

Bone block with the implant was placed into a drying chamber at 70-80°C for 4-5 days. The implant was easily detached from tissues, glycoprotein film on its surface being retained. Optical metallography was carried out and the surface contacting the tissues was mapped.

Corrosion relief was studied by phase contrast microscopy after washing the implant from glycoprotein films in distilled water. High-dose ionic implantation (HDII) of the surfaces of dental device with shape memory, studies of the surfaces of specimens and element composition of biological samples were carried out with participation of L. L. Meisner, Doct. Physical and Mathematical Sciences, at Laboratory of Material Surface Modification Technology, Institute of Strength Physics and Materials Technology, Siberian Division of Russian Academy of Sciences.

RESULTS

The implants surfaces before biological testing varied. Oval depressions of different diameter, depth, and density were present on the surfaces of specimens Nos. 1, 2, and 3. Crater-like depressions 30-40 μ in diameter predominated on the surface of specimen No. 1, depressions 50-70 μ in diameter on specimens Nos. 2 and 3. The number of crater-like depressions 1-2 μ in diameter was the same on the implant surfaces. The surface relief of samples treated by an electron beam has formed during rapid solidification from the liquid phase (a thin layer of the implant material melted by the electron beam).

Honeycomb surface relief of sample No. 4 was due to structure of titanium nickelide alloy with high-temperature shape memory effect. At 25°C this alloy was in the martensite state with B 19' martensite structure.

Traces of mechanical grinding lines and solitary punctate depressions were seen on the surface of sample No. 5. Optically transparent glycoprotein films on the reflecting surface of the implant, isolated from the bone, were detected by phase contrast high resolution optical microscopy (optical differentiation interference contrast method).

The surfaces of implants Nos. 1 and 5 were covered ($^2/_3$ of the surface) with an organic film

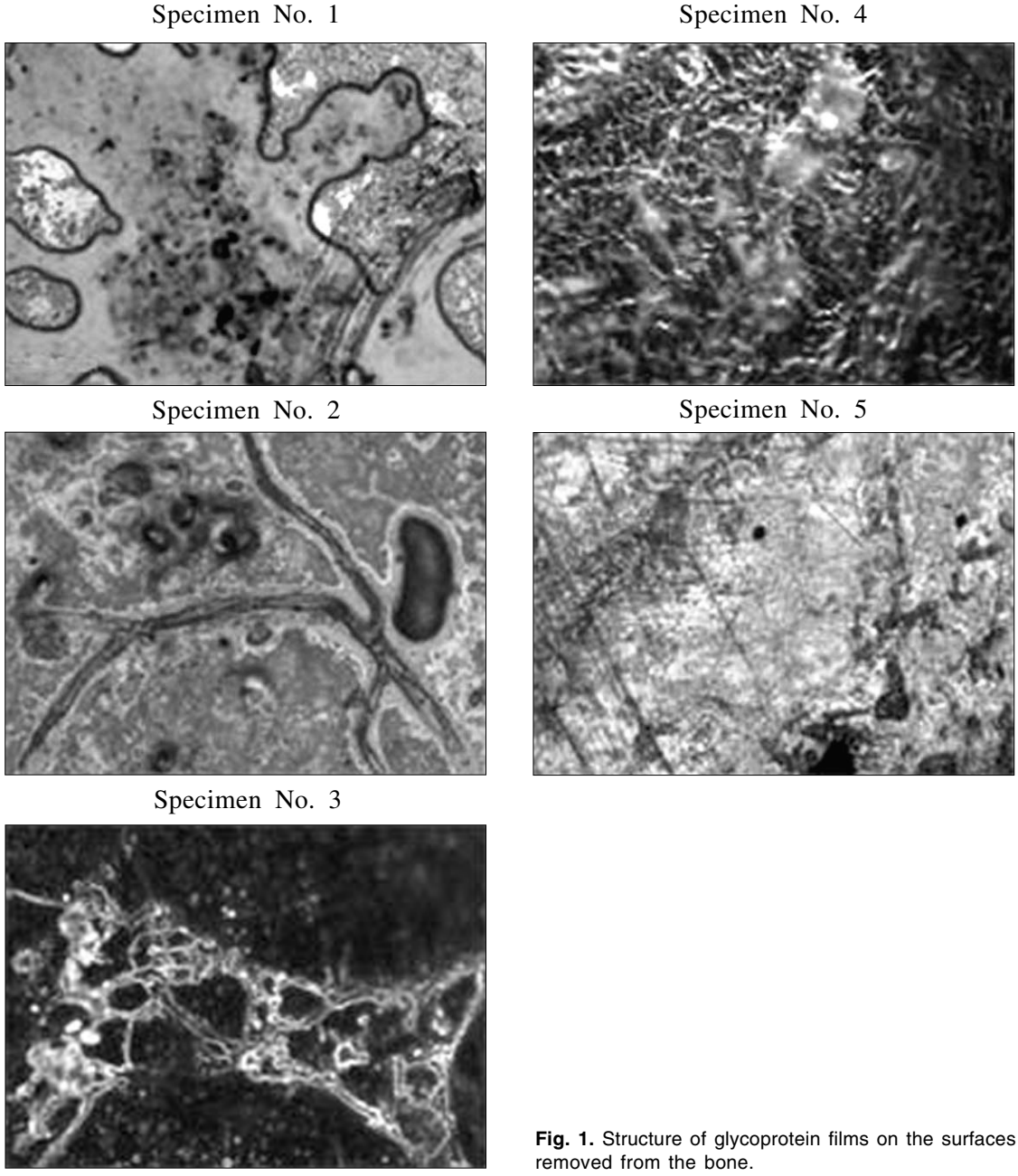

Fig. 1. Structure of glycoprotein films on the surfaces of implants removed from the bone.

presenting as grayish-black blots 1-2 μ thick with clear-cut borders. This coating was present in all crater-like depressions. One-third of the surface was covered by an iridescent film with blurred border, up to 1 μ thick.

The optical picture of film coating of implant No. 2 was heterogeneous. There were areas of round formations of 3 to 20 μ in size, foci of thick film presenting as blots, and granular areas crossed by 20 μ thick dendritic fibrils, and thick films filling the crater-like depressions.

The surface of implant No. 3 was virtually quite free from organic film coating. Small areas were covered by a film constituting an intricate pattern or droplet-like accumulations.

The surface of implant No. 4 had a characteristic martensite relief, honeycomb depressions were filled by fine films. Compact organic films were detected rarely (Fig. 1).

Comparison of the surfaces of specimens washed from organic films showed that pitting corrosion was the most characteristic of all specimens from titanium nickelide alloy with surfaces modified by different methods: it was detected on specimens Nos. 1 and 2 as etching depressions (zirconium ion modification of surface). Specimens Nos.

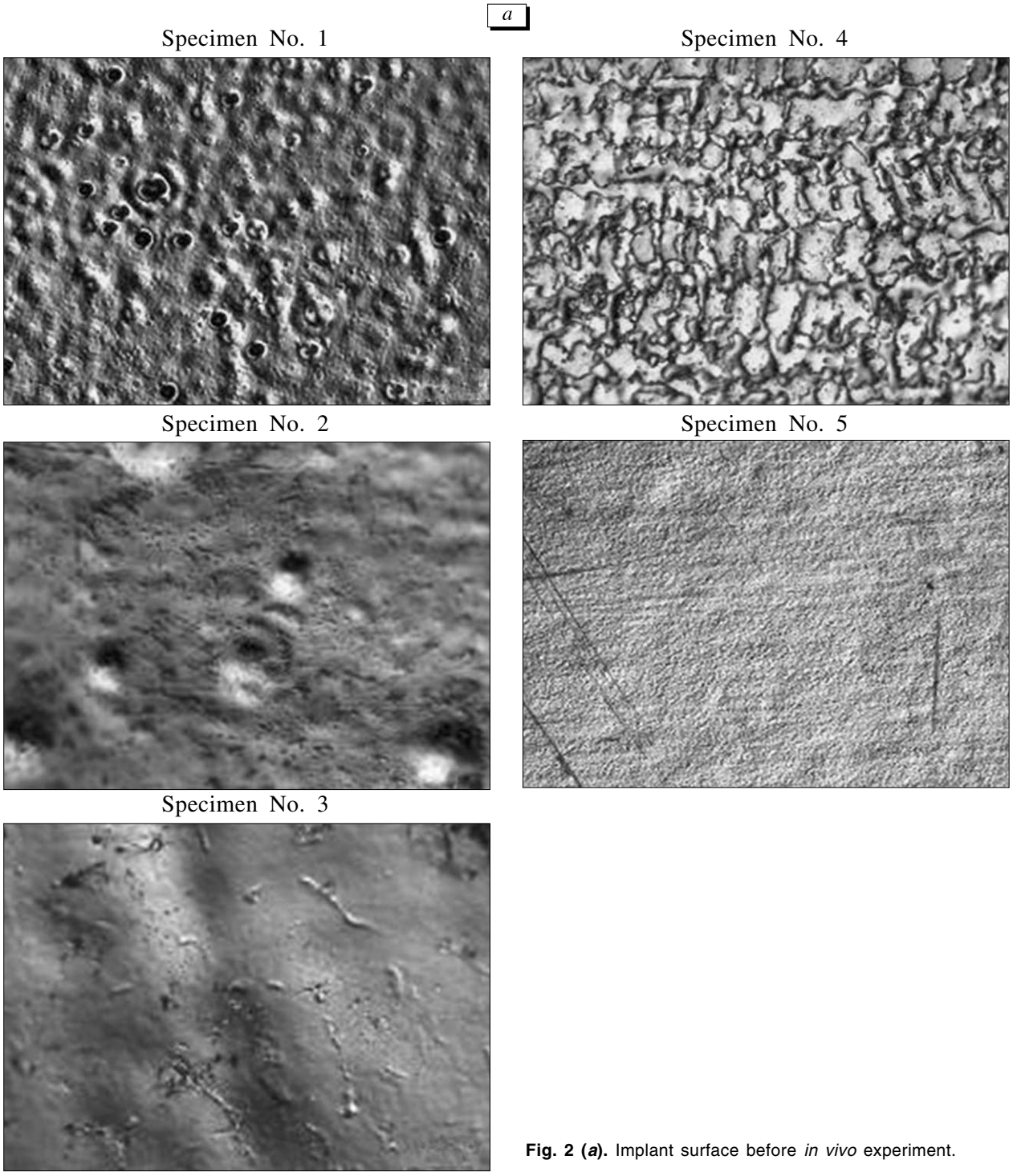

Fig. 2 (*a*). Implant surface before *in vivo* experiment.

3 and 4 exhibited the best corrosion resistance. Despite morphologically developed intricate surface of specimen No. 4, which was in a martensite state, there were just rare traces of pitting corrosion, no corrosion processes being detected at the periphery of the martensite domains.

Corrosion presenting by erosion foci was seen on the surface of implant No. 5. Obvious pitting corrosion with high density of etching pits, which fused and form a deeper corrosion relief (depressions) was seen in such a spot (Fig. 2, *a* and 2, *b*).

The concentration of titanium in specimen No. 5 capsule and adjacent bone surpassed the control values by 40% (capsule) and 20% (bone). The content of titanium in the capsule of specimen No. 1 was 15% elevated, in the bone 5% elevated, the

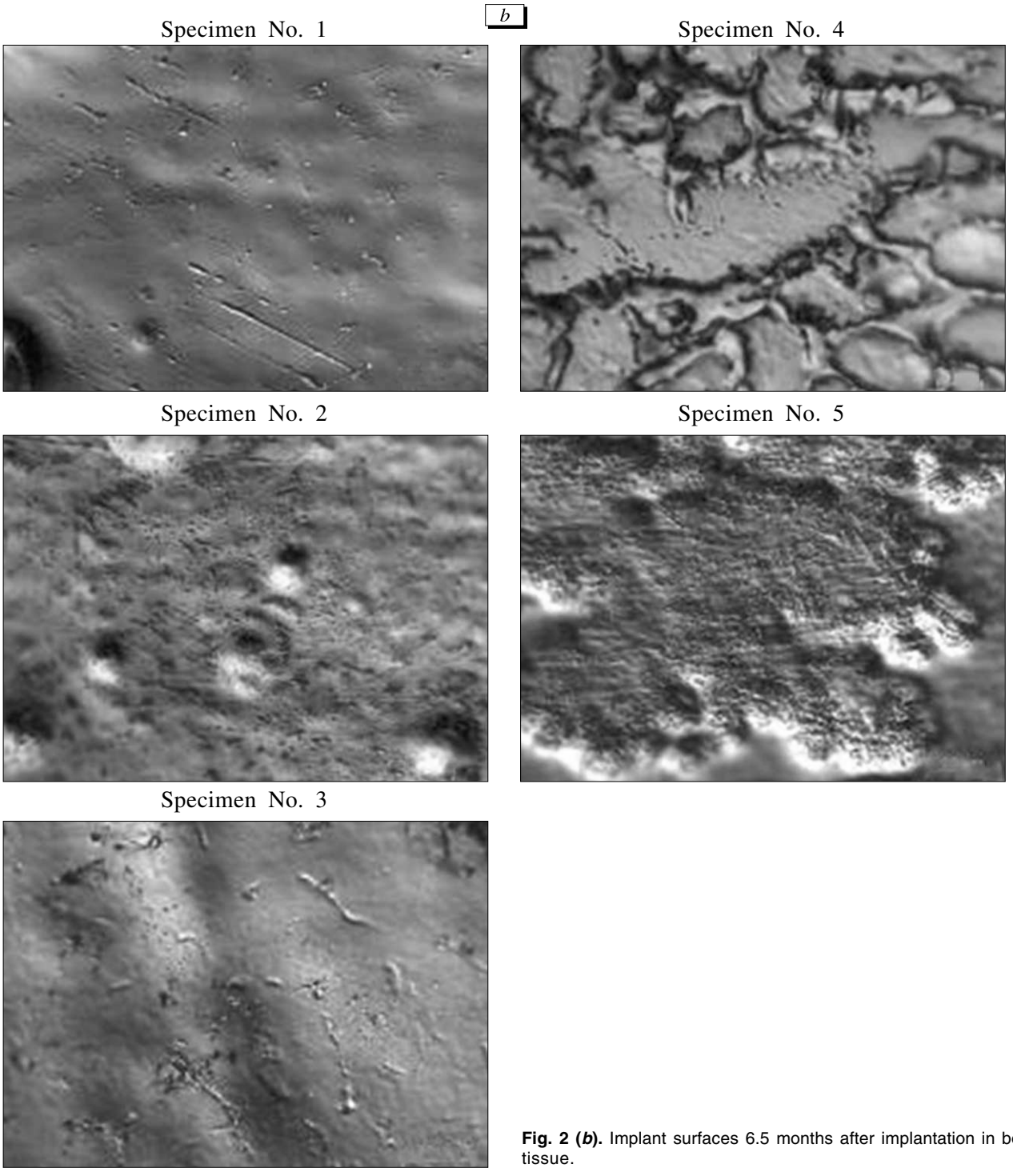

Fig. 2 (*b*). Implant surfaces 6.5 months after implantation in bone tissue.

content of nickel in the capsule being 18% and in the bone 6% higher than in the control.

The concentrations of titanium and nickel in tissues adjacent to specimens Nos. 2, 3, and 4 surpassed the normal values by 5% (capsule) and by 2% (bone). The content of silver was no more than 2% elevated in the capsule and up to 1% elevated in the bone. No increase in the concentrations of zirconium and molybdenum was detected in the bone. The results of chemical analysis of the main elements in organs and tissues of experimental animals (χ^2=6.89, p>0.1) were analyzed. The concentrations of titanium, nickel, zirconium, silver, and molybdenum were not elevated in the organs in comparison with the normal values. The parameters of the main chemical elements involved in

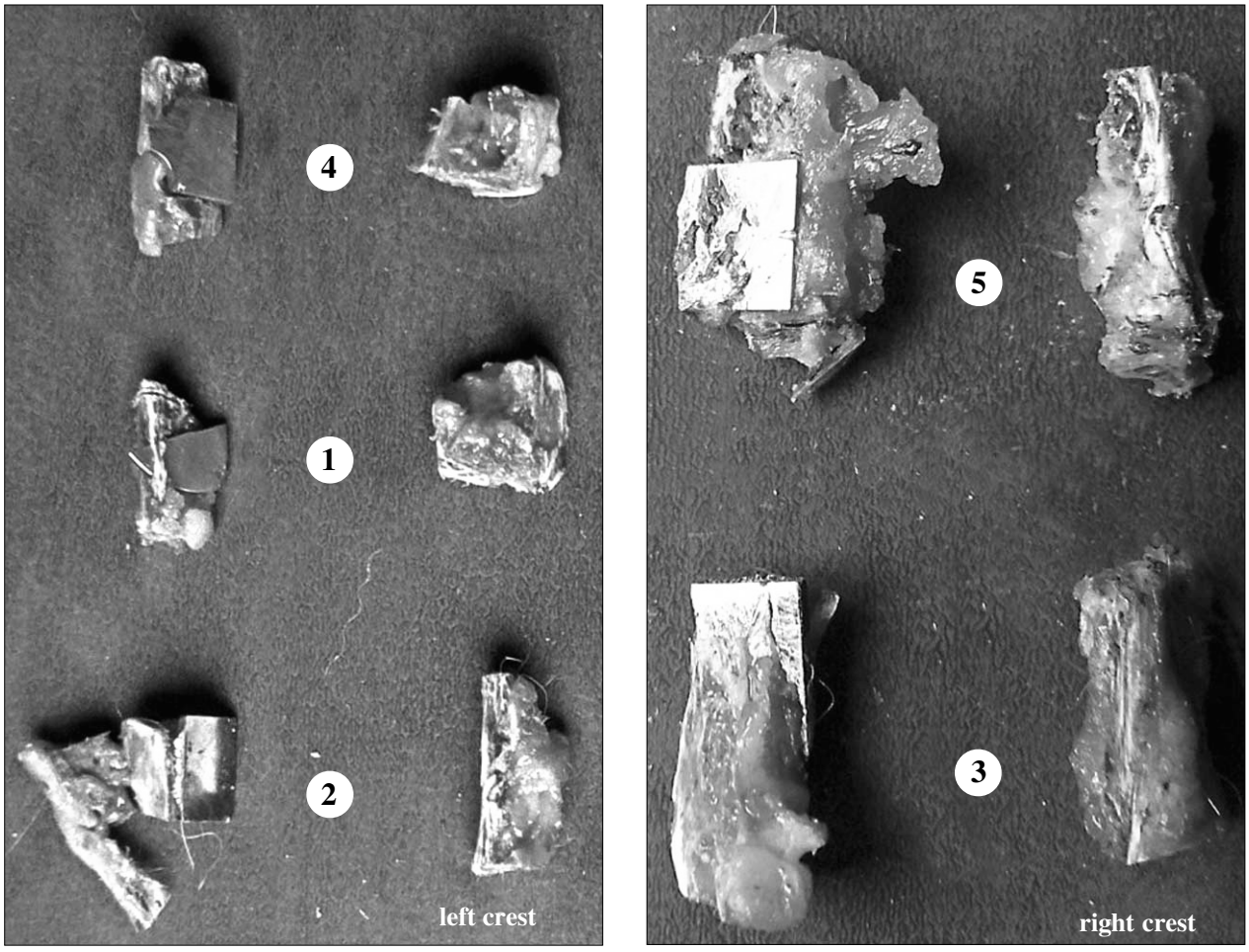

Fig. 3. Macropreparations of bone blocks with the adjacent implants.

biochemical processes of a living body were not disturbed.

Tissues formed around the implanted specimens differed at the level of visual inspection (Fig. 3). Implants Nos. 4 and 2 were surrounded by normal mineralized bone. A rough fibrous cartilaginous capsule enveloped the migrated implant No. 1. Fine connective tissue capsule enveloped specimen No. 1 with resistant bone. The fibers in the underlying bone were coarse, the structure of spongy bone was large-cellular. Implants Nos. 3 and 5 were enveloped in a cicatricial cartilaginous membrane.

The most unfavorable tissue reaction was observed around implant No. 3 (HDII: D (Ag^+): fatty restructuring of the red bone marrow with black incorporations and extremely scanty cells and vessels.

Tissue around implant No. 5 presented as a cicatricial capsule with cartilaginous structures. The underlying bone was characterized by a chaotic trabecular network, uneven mineralization, included cartilaginous cells.

The most favorable reaction of tissues was seen around specimens No. 4 (HDII: D (Mo^+). The fibrous capsule was extremely fine, the adjacent bone had normal structure.

Implants No. 2 (HDII: D (Zr^+) were enveloped in a fine fibrous capsule; the cortical bone was characterized by high mineralization with scanty cell elements. The spongy bone structure was large-cellular, in some cells the myeloid tissue was replaced by fatty tissue with fibrous formations.

Implantation of specimens from titanium and nickel alloys, weighing 15 g, did not lead to an increase in the concentrations of metal ions in the organs and did not modify the functions of the organism.

The least concentration of ions was recorded for the capsule and bone around the implants with modified surfaces $Ti_{50}Ni_{44}Zr_6$ (HDII): D (Mo^+)= 205×10^{17} ion/cm^2 and $Ti_{49.6}Ni_{50.4}$ (1L) (HDII): D (Zr^+)=1.4×10^{17} ion/cm^2, which corresponded to the metallographic picture of surfaces with signs of the minimum pitting corrosion. Bone of normal struc-

ture formed around the implants. Modification (HDII Ag^+) led to suppression of the red bone marrow.

A cicatricial cartilaginous capsule with high concentrations of titanium ions (40-fold surpassing the normal value) enveloped implants from VT-8 alloy; the implant corrosion manifested by erosive foci.

The structure of the capsule and adjacent bone depended on the level of primary stabilization of the implant in the bone bed. A cicatricial cartilaginous membrane formed around the migrated implant; bone tissue incorporated cartilaginous cells and had chaotic foci of mineralization. Stabilized implants No. 1 were enveloped in fine fibrous capsule and the adjacent bone tissue had rough fibers.

Hence, implants with surface modified by molybdenum and zirconium demonstrated maximum biological compatibility in living body. Corrosion resistance of implants from VT-8 alloys was minimum. Surface modification by silver ions suppressed red bone marrow inducing its fatty degeneration.

The presence of 15-g implants from VT-8 nickelide and TiNi in the body for 6.5 months did not lead to elevation of the concentrations of elements of the implant and caused no shifts in the element composition of the parenchymatous organs.

The efficiency of dentures with intermediate support on the intraosseous implants depends, among other things, on high inertness of the material of the denture in active biological environment under conditions of contact with the denture materials. Titanium nickelide alloy with surface modified by molybdenum ions, exhibiting high corrosion resistance, biocompatibility, and not toxic, is a perspective alloy for dentures.

REFERENCES

1. *Biocompatible Materials with Shape Memory and New Technologies in Medicine*, Ed. V. E. Gyunter [in Russian], Tomsk (2004).
2. V. E. Gyunger, *Ros. Vestn. Dental. Implantol.*, No. 2, suppl. 2 (2003).
3. V. K. Leontyev, S. D. Litvinov, and T. V. Sudakova, *Ibid.*, No. 2, 10-19.
4. L. L. Meisner, V. P. Sivokha, A. I. Lotkov, *et al.*, *Materialovedenie*, No. 4, 43-47 (2003).
5. V. N. Olesova, Ya. Yu. Sidorova, and A. I. Pozdeev, *Ros. Vestn. Dental. Implantol.*, No. 2, 12-16 (2004).
6. R. G. Khafizov, *Ros. Stomat. Zh.* No. 2, 31-33 (2000).