Fretting Wear of NiTi - Shape-Memory Alloy

Marcin Klekotka and Jan Ryszard Dąbrowski(✉)

Department of Materials and Biomedical Engineering,
Bialystok University of Technology, Wiejska 45 C, 15-351 Bialystok, Poland
{m.klekotka,j.dabrowski}@pb.edu.pl

Abstract. This study presents the results of tests of friction processes and fretting wear of NiTi shape-memory alloy, which is used in orthodontics and surgery. This research problem is significant because nickel ions released as a result of nitinol wear exhibit toxic action in the human body. Knowledge about wear mechanisms will allow for more effective prevention of processes leading to the destruction of elements of medical constructions and extend the time of their safe operation. Tests were performed on a pin-on-disc fretting tester under dry friction conditions and in a simulated oral cavity environment. Wear assessments were conducted on the basis of microscopy (SEM, TEM, CLM). Obtained results indicate that friction conditions have a significant impact on the mechanism of fretting wear, which is primarily related to oxidation and phase transformation of nitinol.

Keywords: Fretting · Nitinol · Saliva · Wear · Biomaterials

1 Introduction

Shape-memory alloys are among the group of smart materials and are finding ever broader and growing applications in medicine. Nickel-titanium alloys, with a near-equiatomic chemical composition, are used most commonly. Orthodontic wires and arches, as well as braces, intramedullary rods and implants for treatment of spinal defects, among other things, are made from these alloys. The shape-memory effect of nitinol is related to its thermo-elastic martensitic transformation, however, in medical applications, the phenomenon of superelasticity is most frequently used. This transformation is reversible, however exceeding the yield point of strain-induced martensite leads to loss of the material's superelastic properties [1–3].

Reports in the literature indicate that nitinol alloys are susceptible to tribological wear. This particularly pertains to adhesive grafts, which significantly limit the application of titanium alloys in friction pairs [4,5]. However, it must be noted that fretting wear mechanisms of nitinol have not sufficiently been described in the professional literature, and strain-induced phase transformations have a significant impact on wear kinetics [6]. The susceptibility of nickel-titanium alloys to fretting-corrosion processes is also a significant problem [7,8].

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Due to its high nickel content, wear products of nitinol are particularly hazardous to the human body, which is why more shape-memory alloys with similar functional parameters are continuously being sought. Nickel is one of the most common allergens. 10 % of the population is allergic to this metal [9,10]. It has been demonstrated that nickel ions induce lipid peroxidation and inhibit blood platelet aggregation. This process can be held back by means of ascorbic acid. Nickel may also induce a series of carcinogenic processes, and chronic exposure to excessive nickel doses may also weaken innate immunity [11]. It seems that, in light of the above, the planned tests of friction and fretting wear of alloys of this type will bring cognitive and utilitarian value in the context of the application of these materials in medical constructions, particularly orthodontic appliances.

2 Material and Test Methodology

Fretting tests were performed using a friction tester designed and made at the Department of Materials and Biomedical Engineering of the Bialystok University of Technology, and a detailed description of this tester has been presented in an earlier publication [12].

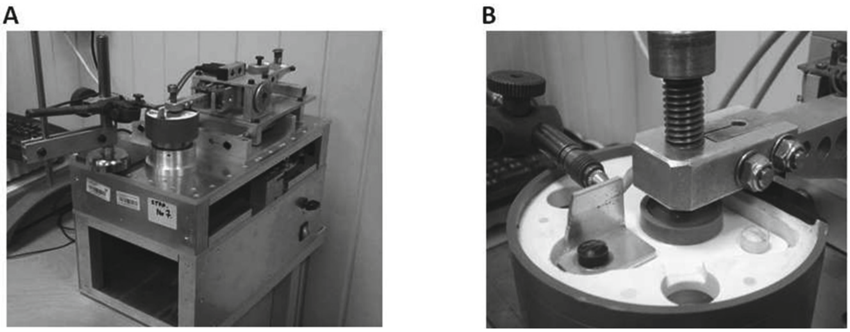

Fig. 1. Research station: A - general view, B - friction pair

Tests were conducted in a pin-on-disc system - Fig. 1. Elements of the kinematic pair were made from NiTi alloy with the following chemical composition: nickel (50.5 % at.), titanium (49.5 % at.). Pins of a cylindrical shape had a 1.1 mm contact surface, and the sample diameter amounted to 4 mm. Sample surfaces were polished mechanically until roughness on the order of $Ra = 0.4\mu m$ was achieved. To remove contaminants, pins and discs were immersed in ethanol and placed in an ultrasound bath for 10 min. After this period of time, samples were thoroughly rinsed with distilled water and dried. Discs were fastened on the tester's moving table, which performed reciprocating movements. The amplitude of displacement was on the order of 100 µm, frequency - 0.8 Hz, and average unit pressures that were set amounted to 5, 15 and 30 MPa. Friction was applied for one hour (2880 cycles) under dry friction conditions and in the environment of human saliva, respectively. Saliva was collected in fasting condition from a 28-year-old healthy man according to a previously developed collection methodology [13]. Each test was repeated 3 times for statistical purposes.

Observations of sample surfaces were conducted using a confocal microscope (CLM, Olympus Lext OLS4000) with 3D imaging capability and a scanning electron microscope (SEM, Hitachi S-3000N). Fretting wear products were observed using a transmission electron microscope (TEM, Tecnai G2 X-TWIN). The application of a confocal microscope made it possible to measure wear and evaluate volumes of lost material and material accumulated over the course of the friction process. Measurements were conducted according to a previously developed research methodology [14]. The chemical composition of the surfaces of friction traces was assessed using an EDS (energy dispersive spectroscopy) module in the scanning microscope.

3 Results and Discussion

Fretting tests were commenced by taking measurements of friction forces in selected friction pairs. This made it possible to determine changes of the coefficient of friction over time at the set unit pressures (Fig. 2).

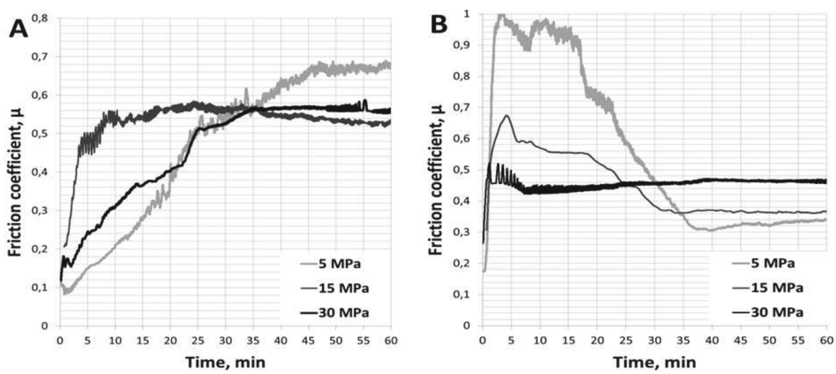

Fig. 2. Changes in coefficient of friction over time: A - under dry friction conditions, B - in the environment of saliva

Nickel-titanium alloys are a characteristic material capable of phase transformations as a result of applied stress (psuedoelasticity) or temperature changes. Data in the literature confirms that the application of strain to the alloy while it is in an austenitic state leads to its martensitic transformation, which is irreversible after the yield point of strain-induced martensite is exceeded [1]. The results presented in Fig. 2 show that, under dry friction conditions, the resistance to motion of kinematic pairs after one hour of friction is the greatest at low unit pressures (5 MPa). However, an inverse phenomenon can be observed in the environment of saliva. When interpreting test results, one should remember that friction is a complex process accompanied by many overlapping mechanisms. Besides phase transformations of nitinol, ingredients of saliva, particularly mucins, may also have an influence on friction. Oxidation processes of nickel and titanium should also be accounted for, as illustrated by the data presented in Fig. 3.

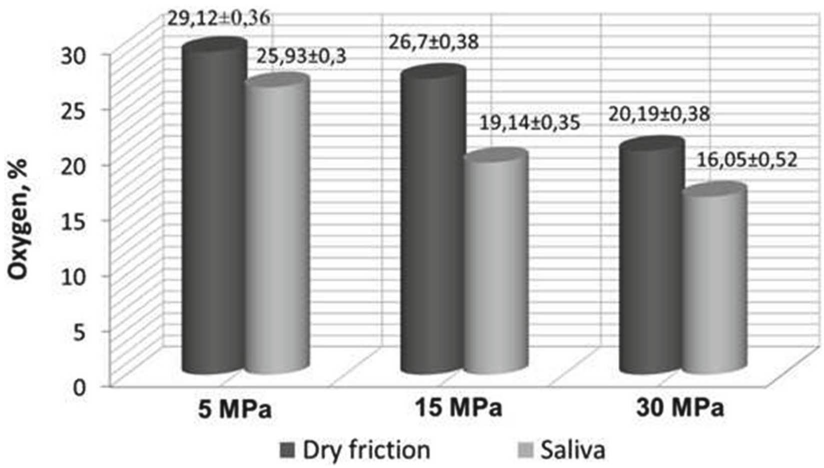

Fig. 3. Oxygen content in wear products

Conducted research indicates that fretting fosters the formation of oxides, and the amount of oxides has a significant impact on friction conditions. In the environment of saliva, where oxygen access was limited, the application of stresses leads to transformation of the soft parent phase (austenite) into the hard martensitic phase, which results in reduction of friction. However, additional structural studies must be carried out to confirm the correctness of this assumption.

Assessment of fretting wear is a complex process, which often takes on a stochastic character. Due to the low amplitude of displacements under fretting conditions, removal of wear products from the friction zone is difficult. Under such conditions, secondary wear may occur, in which formed products act as an abrasive and intensify wear. Due to two-way transport of material between friction surfaces (pin and disc), measurement of material losses is typically insufficient to reflect the actual state of samples. This is why it is indispensable to also account for the volume of accumulations of material permanently affixed to the surface. The results of these measurements have been presented in Fig. 4.

The results of these measurements confirm that susceptibility to adhesive grafts of nitinol increases as load increases. Human saliva is a lubricant that effectively prevents permanent deposition (accumulation) of material on the alloy's

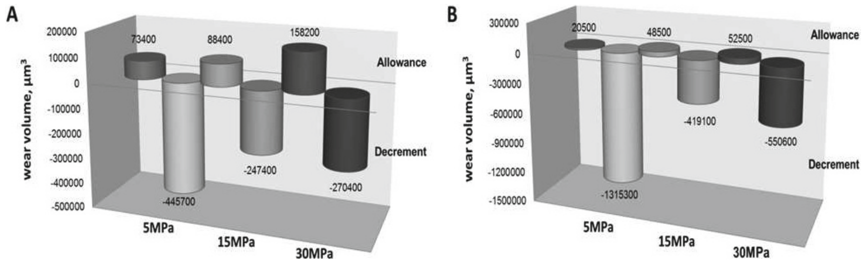

Fig. 4. Fretting wear of disks, accounting for losses and accumulations of material: A - under dry friction conditions, B - in the environment of saliva.

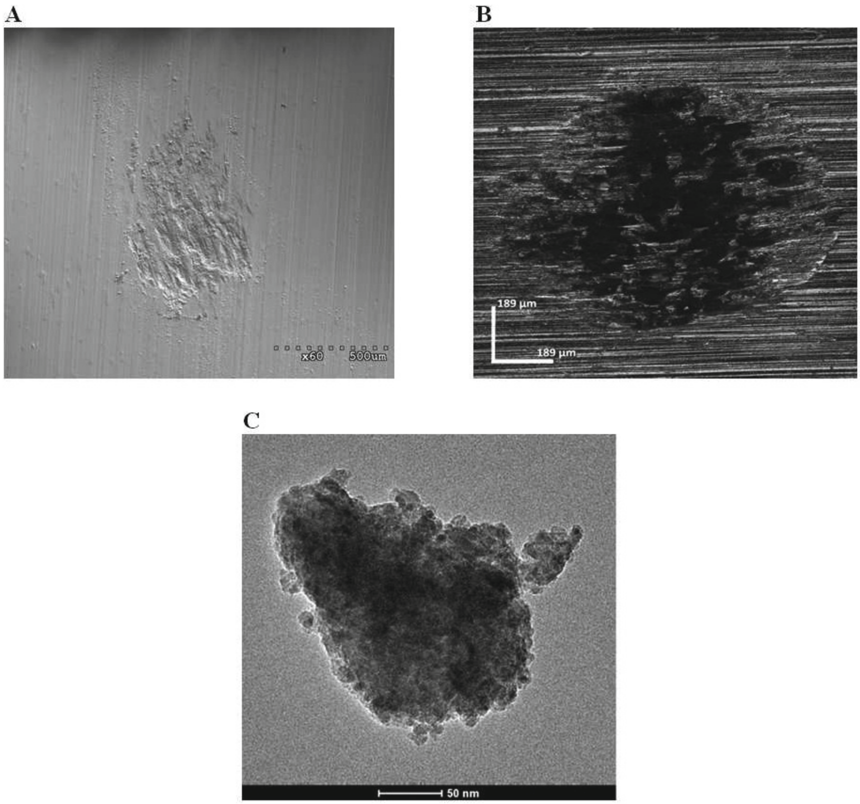

Fig. 5. Photographs of surfaces and products of fretting wear: A - dry friction conditions (SEM), B - in environment of saliva (CLM), C - wear nano-products (TEM)

surface, however, it still intensifies wear in terms of volume (losses), particularly at low unit pressures. This is presumably related to the fact that less energy is supplied to the contact zone, required for the martensitic transformation to occur (longer time of transformation). Figure 5 presents photographs of the

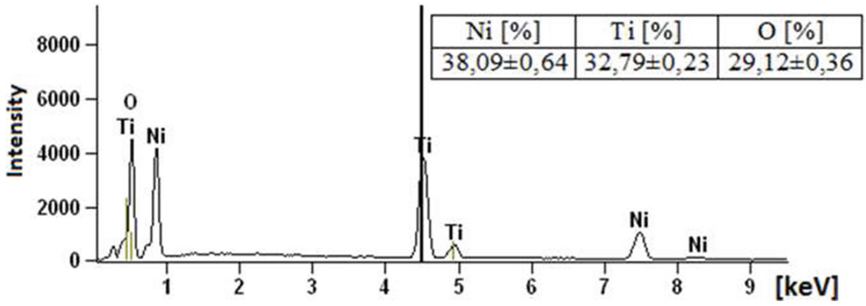

Fig. 6. Chemical composition of wear products on friction surface.

friction surface, with visible wear products. The presence of nanoparticles in the friction zone was confirmed (Fig. 5C) and was also observed in previously conducted tests of this type [15].

Analysis of the chemical composition of wear products (SEM, EDS) confirmed the presence of nickel, titanium and oxygen, which clearly indicates intensive oxidation of the alloy's ingredients during friction - Fig. 6.

4 Conclusions

Obtained test results demonstrated susceptibility to wear of nitinol under fretting conditions. Knowledge about wear mechanisms of biomaterials used in elements of medical constructions may contribute to their effective safeguarding against destruction, and thus extend the lifetime of medical constructions. Fretting processes are characterized by a low amplitude and high frequency of movement between contacting elements, which takes place in many medical constructions, particularly orthodontic appliances. Metal oxides are the most frequently occurring wear products. Their presence in the friction zone may lead to intensification of wear as a result of abrasion (so-called secondary wear), and high unit pressures are the cause of adhesive grafts onto the kinematic pair.

In the case of shape-memory alloys, their phase transformations must also be taken into consideration. As a result of energy supplied in the form of heat or applied stress, the martensitic transformation may occur, which usually leads to a change in the character of wear. Moreover, reports in the literature indicate a problem related to the susceptibility of nickel-titanium alloys to fretting-corrosion processes [8]. Further tests and analysis of these processes may bring measurable benefits, in terms of both knowledge and utility.

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