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BIOCORROSION BEHAVIOR OF A DENTAL SHAPE MEMORY ALLOY

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ABSTRACT

Designing shape memory alloys (SMAs) with suitable mechanical properties, playing a predominant role as functional biomaterials and targeted degradation behavior has been a goal in recent time. Biocompatibility within the human body environment is the essential requirement of metals and their alloys used in reconstructive surgery, such as dental implants. In this research, a cooper based SMA was proposed to replace the most common dental bronze, benefit of unique property of pseudo-elasticity. Therefore, alloys that performs well in the air being inert or passive, may suffer a severe corrosion in the body. Bio-corrosion is accelerated by aqueous ions inside the complex biomechanical system displayed by various parts of human body. The microstructure and bio-corrosion behaviors of the SMA alloy in NaCl aqueous solution have been systematically investigated for nine years. The surface morphology of the resulted specimens was investigated using scanning electron microscopy (SEM) equipped with an energy dispersive spectrometry (EDX). Electrochemical tests were conducted using simulated body fluid (SBF) solution.

KEYWORDS: metallic biomaterials, biocompatibility, corrosion, shape memory alloy and cooper based SMA

1. Introduction

Cu-based alloys, especially Cu-Al-Ni SMAs, are currently being developed as an alternative to the first worldwide known and used in a broad range of biological applications, Ti-Ni. They can exhibit good properties like a large super-elastic window as well as a small thermal hysteresis concomitant with the remarkably high corrosion resistance [1-6]. Furthermore, for a few years it has also been established that the pseudo-elastic and shape memory effects are very competitive, being an advantage over the expensive Ti-Ni SMAs [7]. During the quenching process of the Cu-Al-Ni SMAs, the martensitic transformation exhibited from β-phase to a close packed structure. In the CuAl13Ni4 alloy, two types of thermal induced martensites (β1 and γ1) prevail on this specific alloy composition. The memory properties occur based on crystallographic reversible thermo-elastic martensitic transformation being stable upon cycling in these ternary alloys [1, 7]. In recent years, Cu-Al-Ni shape memory alloys have attracted a lot of interests due to their high strength and good corrosion resistance. Since 2009, an SMA alloy of very close composition has been investigated as material for biomedical applications [8]. Cu–Al–Ni thin ribbons produced by rapid solidification in martensitic state suggest improvement of the corrosion stability and biocompatibility in vitro as compared with dendritic microstructure in cast state. The reason of this paper is to study bio-corrosion for the replacement of the CuAl11Ni4 (ORCAST or NPG brands) an alloy commonly used in dentistry, with an SMA of the same system, CuAl13Ni4. The content of 13 wt.% Al produced satisfactory shape memory properties: pseudo-elastic behavior - allows deformations at body temperature without exerting stress on the oral tissues and damping property - due to their shape recovery under tension and compression loading [9].

2. Experimental procedure

The research program has used samples made from CuAl13Ni4 polycrystalline shape memory alloy. The overall chemical composition was determined by automatic spectrophotometry type Quantovac as: Cu balance, Al 12.88, Ni 4.00, Mn 0.09, Si 0.04, Sn 0.02, Pb 0.01 wt.%. The corroded specimen surfaces examined were in cast, quenched, rolled and extruded state. The proposed CuAl13Ni4 biomaterial was cast in the same mold prepared as for real dental pivot (ORCAST alloy) used in dentistry. The mold containing the hot pivot obtained by centrifugal casting was suddenly cooled in an ice-water container. By quenching, the dendritic structure has become martensitic allowing activation of memory properties. The specimens were immersed each into a glass container containing 0.5 L 0.9% NaCl physiological solution on the 11th of March 2008. The samples were maintained in the corrosion environment, in stagnant conditions at room temperature. The surfaces of the specimens were in state of technological condition, without any preparations, mechanical polishing or chemical etching. Surface morphology of samples was observed using an OLIMPUS BX51 microscope and a Phillips Quanta 200 scanning electron microscope (SEM) coupled with an EDX detector. The electrochemical corrosion of the dental pivot was studied in SBF (a solution that imitates human fluids) on a VoltaLab 21 Electrochemical System (PGP-201).

3. Results and discussion

Results, concerning morphological and structural characterization of surface corrosion are reported in terms of OM images and SEM-EDX date. The corrosion behavior of Cu-Al alloys showed that the addition of aluminum content slightly decreases pseudo-passive current density at the anodic potential [7] being involved in formation of barrier film of Al_2O_3, enhancing of corrosion resistance of these alloys. In this research we propose to increase the aluminum content with 2 wt.%. The main reason for the enhancement of corrosion resistance is formation on the alloy surface of a barrier film of hydrated aluminum oxide/hydroxide, which builds up quickly in salt water. In ternary Cu-Al-Ni alloy is considered that enhancement of corrosion resistance is given by the emergence of duplex layer composed of $Cu_2O \cdot Al_2O_3 \cdot xH_2O$ [7, 8] thin and strongly adherent inner barrier Cu_2O. The existence of Ni leads to the improvement of corrosion resistance, grater with higher Ni content due to the incorporation of Ni into the thin and strongly adherent inner barrier Cu_2O protective film [9]. Ni also is considered to suppress diffusion of Al and Cu [8].

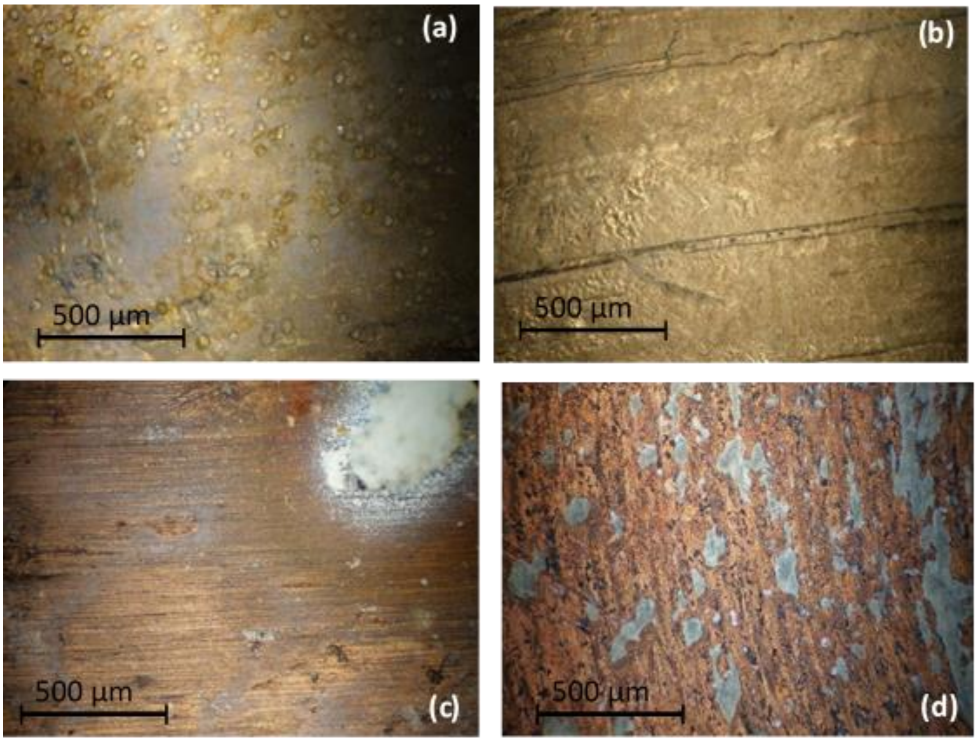

Fig. 1. *OM micrographs of CuAl13Ni4 shape memory alloy in martensitic state of surface after exposure for nine years in NaCl aqueous solution: a) quenched state; b) rolled; c) extruded and d) after electrochemical test in SBF*

Although the alloy is very homogeneous and chemically pure - prerequisite for shape memory properties, surface corrosion after exposure for nine years in NaCl aqueous solution, it is not uniform. The selective oxidation products appear to be specific copper oxide, red or turquoise, yellow (Figure 1c-d) [11]. The gray color is specific to aluminum passivation (Figure 1a). The green and blue colors are specific to nickel oxides and Ni_3Al precipitates in oxidized state (Figure 1a, c and d) [11]. Out of the more important ionic species, only Cl^- has an aggressive behavior in copper corrosion, especially in the "pitting" process. For bio-liquids in the oral cavity, aggressive type ions are much broader considering that a number of other ions enter this environment. In the cast state, as it is now used in dental technology, the alloy is more susceptible to corrosion than in martensitic state because of chemical inhomogeneity associated to dendrite structures [8]. The greatest part of the surface quenched sample is light brownish CuO_2 and gray aluminum oxide, but with blue interpenetration from Ni oxides (Figure 1a). In some areas of specimens, the corrosion products were absent in particular in rolled state (Figure 1b). There can be viewed salt (NaCl) crystals in the form of white crystals colorless. Figure 1d presents the sample studied in SBF solution highlighting red-brownish cooper oxides in strings and gray areas of aluminum oxide. The Penetration Index of 12.11 μm/year, calculated based on linear polarization data, reveals a good stability compared to the behavior of 316L steel in the same solution, which is 438 μm/year [12].

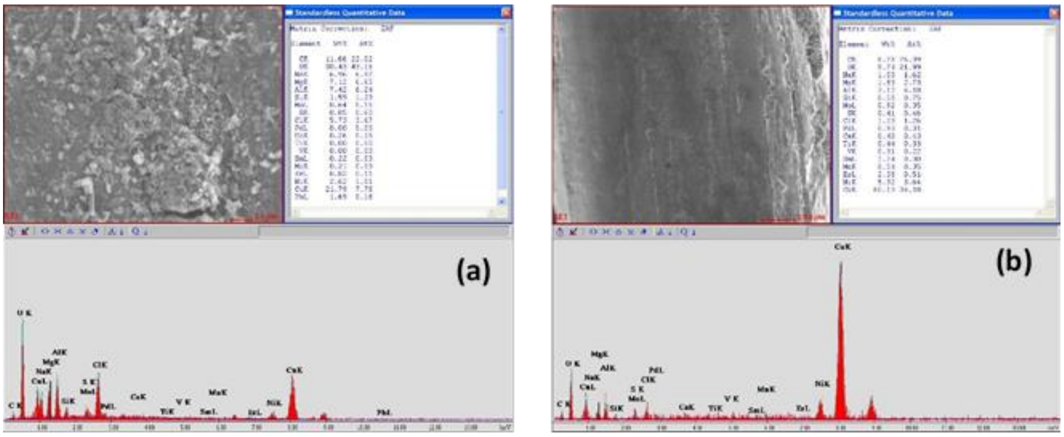

***Fig. 2.** SEM-EDX images to typical surface corrosion of CuAl13Ni4 shape memory alloy surface after exposure for nine years in NaCl aqueous solution in quenched state-a) ensemble; b) detail from peripheral area*

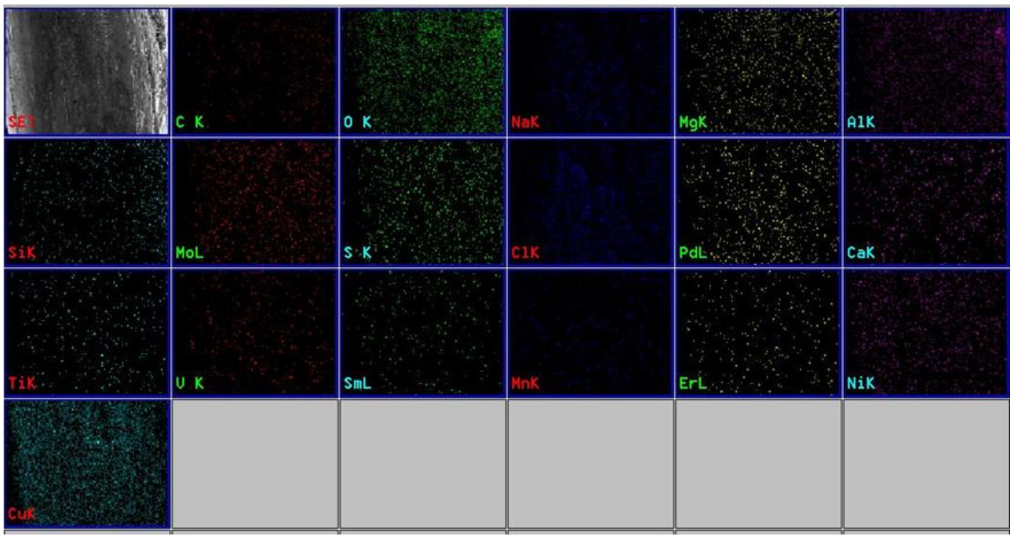

***Fig. 3.** EDX spectrum of CuAl13Ni4 shape memory alloy surface after exposure for nine years in NaCl aqueous solution in quenched state: elemental map*

SEM observations (Figure 2) showed the morphology of oxidation $CuAl_{13}Ni_4$ shape memory alloy surface after exposure for nine years in NaCl aqueous solution in quenched state on which fine and ordered structure was allowed, being chemical homogenous. The area viewed in Figure 2a presented EDX highest picks for oxygen, aluminum, chlorine and sodium, but cooper pick reaches only 21.79%. The enlarged detailed image b presented EDX highest picks for cooper and oxygen, most probably porous Cu_2O film. The elemental mapping regions from Figure 2b and corresponding mappings of elements are presented in Figure 3. EDX spectrum of CuAl13Ni4 shape memory alloy surface after exposure for nine years in NaCl aqueous solution in quenched state as qualitative analysis identify Cu, Al and Ni elements showing a fairly uniform distribution. It is obvious that the oxygen reached areas are present only on the corroded surface indicating the formation of oxide layer. Chlorine and sodium atoms are dispersed on surface, too.

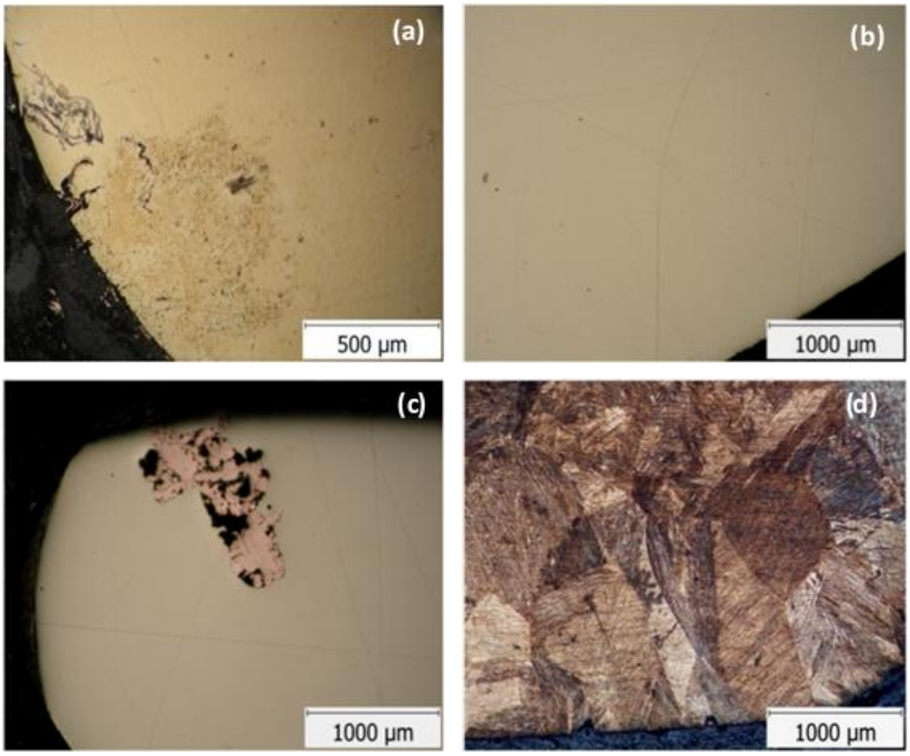

Fig. 4. *OM micrographs of CuAl13Ni4 shape memory alloy the surface cross section after exposure for nine years in NaCl aqueous solution: a) cast state; b) and c) quenched; d) etched with $FeCl_3$ in quenched state*

In Figure 4 is presented the surface cross section after almost 8 years for cast state and quenched samples. The mainly surface cross section aspect of all sample studied looks almost uncorded except dendritic, eutectoid or structure with grain boundaries precipitate. As can be seen from images, initiation of corrosion process occurs on scratch remaining after processing. The crevice corrosion is manifested as a result of water capillarity action inside micro-cracks. The quenched dental pivot had good corrosion behavior as can be seen from Figure 4b and c. The only crevice allowed seepage under oxide film on grains boundaries and occasionally inside whole grains. The grains that are etched at grains boundaries became pink colored. When the gap is larger, an inside deep corrosion takes place. If the surface after processing would be polished as the dental technology requires, the corrosion resistant would be improved over the dendritic or eutectoid structure. The corroded sample in quenched state polished and etched with $FeCl_3$ reveals fine martensite needles inside large austenitic grains.

4. Conclusion

This study comes on a long term, about 9 years, and analyses corrosion behavior in NaCl aqueous solution of a $CuAl_{13}Ni_4$ shape memory alloy after casting, quenching and plastic deformation processes. The alloy highlights a good corrosion behavior in martensitic quenched state after centrifugal casting.

The OM, SEM, EDX reveal the protection of oxide films and initiation and growth of corrosion products. The study confirmed that centrifugal casting followed by quenching enables the production of $CuA_{13}Ni_4$ dental pivots with the shape memory effects which exhibit higher resistance to corrosion than a mould cast alloy ($CuAl_{11}Ni_4$) used in dentistry. The corrosion behavior of shape memory dental pivots in salt water may be improved by polishing the uneven surfaces.

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