Microstructure and Properties of Plasma Spray Coatings Prepared from Ti-Zr-Ni Quasicrystalline Powders

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Abstract

Ti-Zr-Ni coatings deposited by low vacuum plasma spray technique consisted of nanometer-sized W-$Ti_{50}Zr_{35}Ni_{15}$ 1/1 cubic approximant and TiZrNi Laves phases as well as a low volume fraction of ZrO_2 phase. The shift of composition during deposition of the quasicrystalline powders and the presence of ZrO_2 phases are believed to be responsible for the reduced corrosion performances evaluated by means of electrochemical tests in a Hanks' Balance Salt Solution at 37°C.

Keywords : Titanium, quasicrystal, plasma spray coating, microhardness, corrosion

1. Introduction

Titanium alloys have emerged as the most promising candidates for the realization of highly biocompatible implant materials. However, it has been recognized that, in the long term, these implants and particularly orthopedic implants may be associated with adverse local and remote tissue reactivities in some individuals as a consequence of surface degradation. There is thus a need for the development of new coating materials, and this works was an attempt to investigate the performances of layers composed of aperiodic structures.

$Ti_{45}Zr_{38}Ni_{17}$ icosahedral quasicrystalline (QC) powders were prepared by gas atomization method and deposited onto Al substrates by low vacuum plasma spray technique. The microstructure of the coating layers was observed by X-ray diffraction and transmission electron microscopy. We present the microhardness and corrosion properties evaluated by DC polarization technique in a simulated physiological Hanks' balance salt solution at 37°C.

2. Experimental and Results

$Ti_{45}Zr_{38}Ni_{17}$ powders were prepared by gas atomization under a nitrogen atmosphere. Plasma spraying of powders with size range of +38-78μm was performed using a METCO F4-HBS gun in a closed chamber preliminary filled with Ar gas then evacuated by a rotary pump. Powders and coatings were analyzed by means of X-ray diffraction (XRD) (Cu, Kα) and trasmision electron microscope (TEM). The microhardness of the coatings was measured by means of a Vickers microhardness indenter under a load of 50g. The electrochemical properties were investigated in an aerated simulated physiological Hanks' Balance Salt Solution (HBSS) at 37°C.

The gas atomization of melt with composition $Ti_{45}Zr_{38}Ni_{17}$ under N_2 atmosphere resulted in the production of powders with icosahedral QC structure as indicated by XRD analyses. In contrast, the XRD trace of the plasma spray coating layers exhibited broad peaks slightly shifted suggesting the presence of a phase similar to the icosahedral phase with nanometer size, together with additional peaks. A thorough analysis of the XRD traces resulted in the identification of the W-$Ti_{50}Zr_{35}Ni_{15}$, Laves-TiZrNi, and ZrO_2 phases. Using the Sherrer formula, the grain size of the W-$Ti_{50}Zr_{35}Ni_{15}$ phase was estimated to be approximately 90 nm.

TEM observation of the coating layers, as shown in Fig.1, confirmed the nanometer size of the grains identified as the W-$Ti_{50}Zr_{35}Ni_{15}$ and Laves-TiZrNi from analyses of the rings in the slected area electron diffraction patterns (SAEDP). A low volume fraction of isoleated ZrO_2 phase of about 100-300 nm (not shown) was also observed. The presence of this segregated phase inside the coating can be explained by the superficial oxidation of the powders although the deposition was performed under low vacuum.

The absence of icosahedral QC phase in the coating could be attributed to a compositional shift as a consequence of Ti loss by vaporization during heating of the powders in the plasma flame. The shift of composition induced the formation of the W-$Ti_{50}Zr_{35}Ni_{15}$, cubic crystalline phase of space group $Im\bar{3}$ and lattice parameter a = 1.418 nm, which was designated as an approximant phase of the icosahedral QC phase. Approximant phases exhibit characteristics similar to those of QCs owing to the local atomic arrangement according to icosahedral coordination leading to the existence of axis of symmetries such as pseudo 5-fold, pseudo 3-fold and pseudo 2-fold.

QCs are recognized as hard materials with high corrosion resistance [1-3]. The microhardness value of the coatings, average from 10 measurements, was found to be 3.7 ± 0.3 GPa, which is about the microhardness of the cast Co-Cr-Mo alloy and more than twice that of the Ti-6Al-4V alloy.

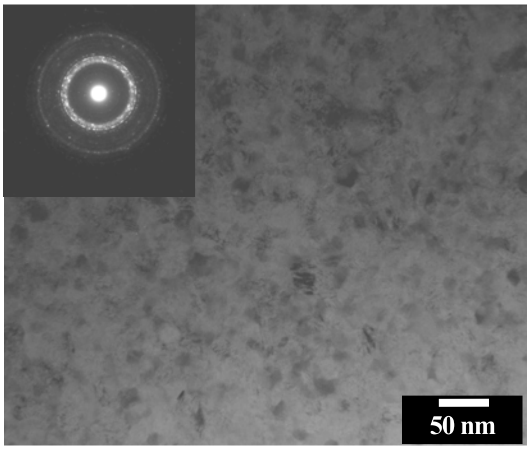

Fig. 1. TEM bright field image of the coating microstructure and SAEDP in inlet.

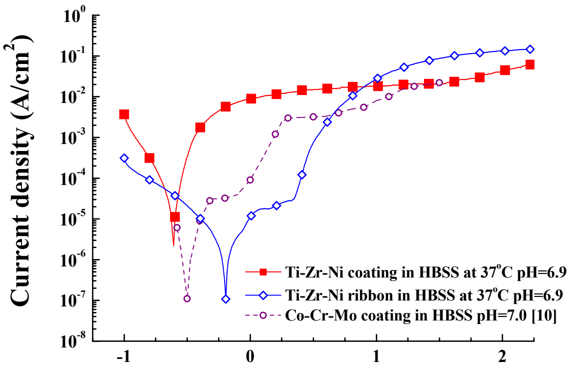

Fig. 2. Variation in current density as a function of the applied potential and comparison with Co-Cr-Mo plasma sprayed coating.

Surface films play a key role on the corrosion behavior and it is acknowledged that Ti oxides, and particularly TiO_2, have a high corrosion resistance in a simulated physiological solution [4]. The potentio-dynamic curve obtained in HBSS is shown in Fig.2, and is compared with those of the rapidly quenched $Ti_{45}Zr_{38}Ni_{17}$ QC ribbon and Co-Cr-mo plasma sprayed coating [5]. The corrosion current density of the Ti-Zr-Ni coating was about 2 orders of magnitude higher than that of the rapidly quenched ribbons and the Co-Cr-Mo plasma sprayed coating. Moreover, the corrosion potential for the coating is significantly lower than that of the QC ribbon indicating a less noble behavior, which can be interpreted by the difference of composition and the presence of defects such as segregations. The shift of composition induced by the loss of Ti is believed to result in the formation of a Zr-rich oxide film on top of the coating layer instead of the Ti-rich oxide. Furthermore, defects such as cracks, splat boundaries and segregations are believed to induce premature localized corrosion damage. It is well known that phases with different compositions exhibit different electrochemical properties, i.e., some are more noble than others. Thus, in the presence of HBSS solution, the isolated ZrO_2 phases are believed to induce a galvanic effect, which would accelerate locally the corrosion process.

3. Summary

Ti-Zr-Ni icosahedral quasicrystalline powders prepared by gas atomization were deposited onto Al substrate by plasma spraying techniques. The vaporization of Ti induced a shift in the composition and resulted in the formation of nanometer-sized W-$Ti_{50}Zr_{35}Ti_{15}$ 1/1 cubic approximant and TiZrNi Laves phases. Because of the high affinity of zirconium for oxygen, submicrometer-sized ZrO_2 phases were also observed in the coating layers although the powders were deposited under a low vacuum. The compositional shift and the presence of isolated ZrO_2 phases combined with the existence of defects inherent to the plasma spray process resulted in a relatively low value of the microhardness and poor corrosion resistance in simulated physiological HBSS solution.

4. Acknowledgements

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5. References

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