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Flexible (Zr,Ti,O) alloy films with enhanced resistance to cracking prepared by magnetron sputtering

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1 Introduction

In recent years, binary zirconium-titanium alloys have been an object of intensive research stimulated by their good mechanical properties such as high strength-to-weight ratio, enhanced corrosion resistance and excellent biocompatibility. According to the phase diagram the ZrTi alloy creates only a solid solution for any composition of the alloy due to almost zero heat of mixing; $\Delta H_{ZrTi} = 0$ for 50 at.% Zr and 50 at.% Ti. Metallurgical processes such as melting and casting create alloys with a macro-sized crystal structure. On the other hand, widely used PVD processes allow to form nanocrystalline and amorphous alloy films. Nanocrystalline alloy films can be easily formed if they are produced under a strong ion bombardment of the growing film, for example, using the ion plating sputtering process. This process is based on the grain refinement by stopping of the grain growth during ion bombardment. The nanocrystallization process can be further enhanced in the case when (i) metalloid atoms (As, Te, Ge, Si, Sb, B) replace one of the metal element (Me_1 or Me_2), i.e. a (Me_1,Met) alloy film is formed, or (ii) a small amount of one of the metal elements (Me_1 or Me_2) in the (Me_1,Me_2) alloy is replaced by a small addition of the reactive gas atoms (O, N, C, etc.), i.e. (Me_1,Me_2,O), (Me_1,Me_2, N), etc. alloy films are formed; here Met is the metalloid atom. For a (Me_1,Me_2) alloy film there are weak metallic bonds between the metal atoms (e.g. the partial cohesive energy 1.3 eV of Zr in hcp Ti in the dilute limit) and a high mobility of atoms on the surface of the growing film, which results in the growth of well-developed crystalline grains. On the contrary, oxide and nitride films have strong metal-oxygen and metal- nitrogen bonds (e.g. 6.86 eV and 4.81 eV for Ti-O and Ti-N, respectively) and thereby the atoms forming molecules exhibit a low mobility on the surface of the growing film. Strong covalent or ionic bonds in materials of such films slow down the motion of individual atoms on their surfaces during their growth and thereby prevent atoms from reaching positions necessary to form a crystalline film. Therefore, the (Me,Met) alloy films containing the metalloid atoms and (Me_1,Me_2) alloy films with added reactive gas atoms, i.e. (Me_1,Me_2,O) or (Me_1,Me_2,N) alloy films with a small addition of O or N, deposited on an unheated substrate, can exhibit strongly nanocrystalline structure and enhanced hardness. In the case when the ratio of Met and Me atoms (Met/Me) is properly selected the (Me,Met) alloy film can exhibit even a fully disordered (X-ray

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amorphous) structure, for instance, the a-(Al,Ti) alloy films in the Al–Ti system or a-(Al,Si) alloy film in the Al-Si alloy system can be formed.

This work shows how (1) the structure of a (Me_1,Me_2) alloy film varies from crystalline to nanocrystalline under ion bombardment and (2) the nanocrystallization of a (Me_1,Me_2) alloy film can be enhanced in the case when a small amount of oxygen is incorporated in the (Me_1,Me_2) alloy, i.e. when a (Me_1,Me_2,O) alloy film is formed. To demonstrate the effect of the ion bombardment on the structure of the (Me_1,Me_2) alloy film, its nanocrystallization and the hardness enhancement in the (Me_1,Me_2,O) alloy film (Zr,Ti) and (Zr,Ti,O) alloy films with three elemental compositions - $Zr_{95}Ti_5$, $Zr_{30}Ti_{70}$ and Zr_5Ti_{95} were selected. The main aim of this work is to show under what conditions it is possible to sputter flexible alloy-based films with enhanced hardness and resistance to cracking.

2 Results and Discussion

The main results of the detailed investigation of the structure, microstructure, physical and mechanical properties of sputtered Zr-Ti alloy films with different elemental composition was summarized by Musil at al. (2017) as follows:

1. All sputtered Zr-Ti films are solid solution films as the binary phase diagram of the (Zr,Ti) alloy predicts.
2. The (Zr,Ti) alloy films with small amount of Ti (≤5 at.%) are the alloy films with the α-Zr phase. On the other hand, the (Zr,Ti) alloy films with high amount of Ti (≥ 70 at.%) are the alloy films with the α-Ti phase.
3. The (Zr,Ti) alloy films are well crystalline and exhibit a strong texture, α-Zr (002) for the $Zr_{95}Ti_5$ film and α-Ti (002) for the $Zr_{30}Ti_{70}$ and Zr_5Ti_{95} films, when they are sputtered at low negative bias $U_s = -50$ V.
4. The crystallinity of the (Zr,Ti) alloy films can be strongly reduced by (i) a strong ion bombardment of the growing films, i.e. when the films are sputtered at high negative substrate biases $|U_s| \geq 150$ V, and (ii) the addition of a small of oxygen into the argon sputtering gas. Both methods allow to form the nanocrystalline Zr-Ti alloy films.
5. The incorporation of a small amount of O (≤ 15 at.%) in (Zr,Ti) alloy film is very effective way to increase its hardness H and to form flexible (Zr,Ti,O) alloy films with enhanced resistance to cracking.
6. The (Zr,Ti,O) alloy films with addition of a small amount of O($\phi_{O2} \leq 2$ sccm) are brittle and easily crack due to low hardness $H < 10$ GPa, low ratio $H/E^* < 0.1$ and low elastic recovery $W_e < 60$ %. On the other hand, the (Zr,Ti,O) alloy films with addition of a higher amount of O ($\phi_{O2} \geq 2$ sccm) exhibit an enhanced resistance to cracking because they have the high hardness $H = 16$ GPa, high ratio $H/E^* \geq 0.1$ and high elastic recovery $W_e \geq 60$ %.

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References

Musil J., Zenkin S., Čerstvý R., Haviar S., Čiperová Z. (2017) (Zr,Ti,O) alloy films with enhanced hardness and resistance to cracking prepared by magnetron sputtering, *Surf. Coatings Technol. 322*, pp. 86–91.