

STRUCTURE AND MICROHARDNESS OF MAGNETRON SPUTTERED ZrCu AND ZrCu-N FILMS

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1. Introduction

In recent years a great attention has been devoted to the preparation and investigation of nanocomposite films which exhibit new mechanical [1], electronic [2,3], magnetic [4] and optical properties due to size dependent phenomena. These films are composed of at least two phases which are mutually immiscible and form very fine dispersions of one phase within a second phase. Individual phases can be two different metals, metal and metal nitride or two different metal nitrides.

Present paper reports on the structure and microhardness of ZrCu and ZrCu-N films. The main goal is to demonstrate that (i) ZrCu films are nanocrystalline because Zr and Cu are immiscible elements and (ii) ZrCu-N compound can form nanocomposite films composed of two ZrN and Cu separate phases.

2. Experimental

The ZrCu and ZrCu-N films were deposited by d.c. sputtering using a conventional planar round magnetron with an alloyed ZrCu (70/30 wt.%) target of diameter 100 mm. The vessel was a stainless steel chamber ($\varnothing=250$ mm, $L=400$ mm) pumped by a turbomolecular pump (150 l/s) to a base pressure of about 7×10^{-4} Pa. After evacuation, Ar or an Ar+N₂ (both of 5 N purity) mixture was introduced into the chamber and all experiments were made at a constant total pressure of 0.7 Pa.

The films were deposited onto polished and ultrasonically precleaned Si(111) plates (13x18x0.4 mm³). The substrate was placed on a movable and heatable substrate holder electrically isolated from the grounded chamber. A shutter placed between the magnetron and substrate holder made it possible to clean the magnetron cathode surface before film deposition. The films were deposited under the following constant parameters: the discharge current $I_d=1$ A, the substrate-to-target distance $d_{s-t}=60$ mm and the total pressure $p_T=0.7$ Pa. A typical thickness of the ZrCu and ZrCu-N films was 3 μ m and 2.3 μ m, respectively.

The film thickness measurement, X-ray diffraction analysis (XRD), computer controlled microhardness testing and chemical composition of the ZrCu films by glow discharge optical emission spectroscopy (GDOES) were performed.

3. Results and discussion

A typical deposition rate of ZrCu films sputter deposited at $I_d=1A$ and $U_s=U_{fl}$ was found to be $0.15 \mu\text{m}/\text{min}$. The deposition rate a_D of ZrCu-N films strongly decreases from $0.15 \mu\text{m}/\text{min}$ at $p_{N_2}=0$ to about $0.05 \mu\text{m}/\text{min}$ at $p_{N_2}=0.05 \text{ Pa}$ and then only very slowly decreases with increasing p_{N_2} . A strong decrease of a_D is due to the covering of the target by an alloy nitride $(\text{ZrCu})\text{N}_x$.

The structure of ZrCu and ZrCu-N films was characterized by XRD patterns. XRD patterns from the ZrCu films sputtered on unheated substrates at U_s ranging from a floating potential U_{fl} up to -700 V exhibited only one, very broad reflection line located at $2\theta=44^\circ$ with FWHM of about 8° , see Fig.1a. An estimation of the grain size from the Scherrer formula shows that the size of grains is of about 2 nm . Such broad peaks are typical for nanocrystalline materials containing small grains.

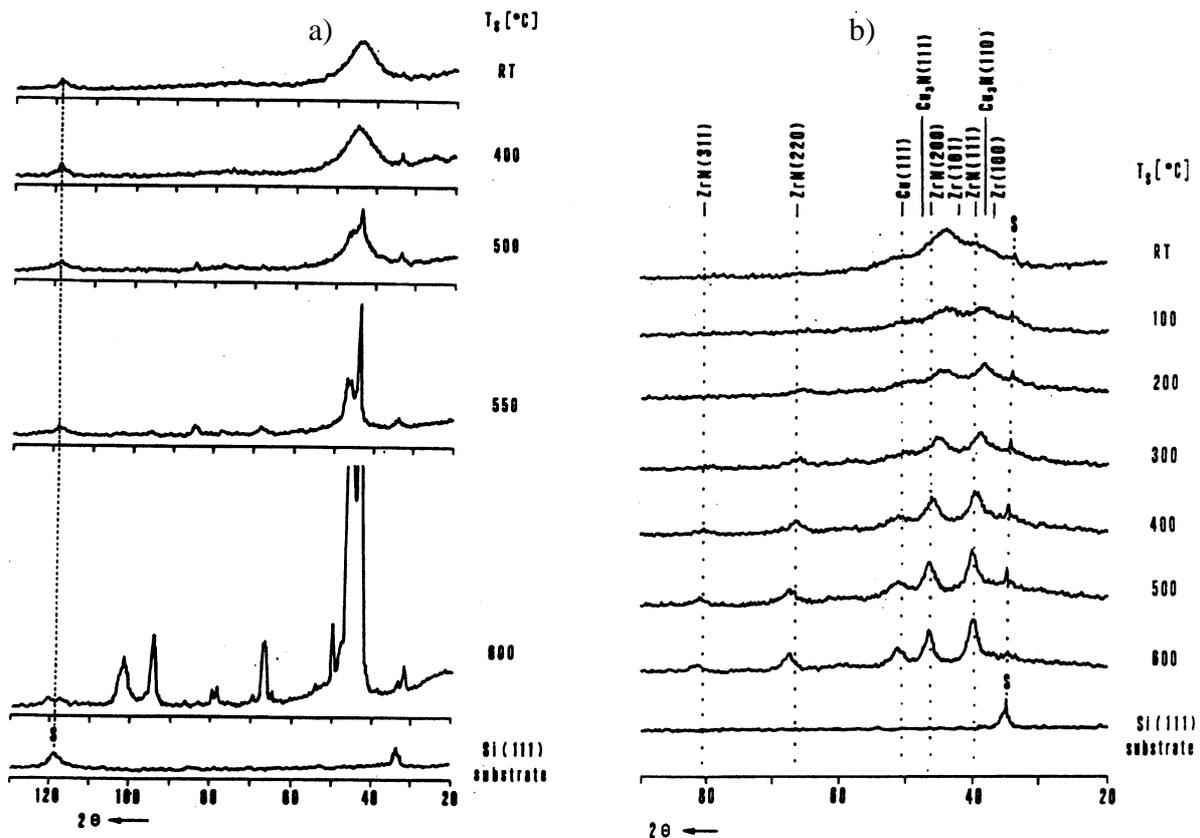


Fig. 1. Development of XRD patterns with increasing substrate temperature T_s : (a) ZrCu films deposited at $I_d=1A$, $p_T=p_{Ar}=0.7 \text{ Pa}$ and $U_s=U_{fl}$; (b) ZrCu-N films deposited at $I_d=1A$, $U_s=U_{fl}$, $p_{N_2}=0.3 \text{ Pa}$ and $p_T=0.7 \text{ Pa}$.

According to GDOES it was found that the chemical composition of the sputtered film is $Zr_{62}Cu_{38}$, i.e. the same as the composition of target. For this chemical composition we can expect, according to an equilibrium phase diagram of ZrCu alloy, that the sputtered ZrCu film contain Zr_2Cu and ZrCu phases. An identification of these phases is now under way.

The ZrCu-N films sputter deposited on heated substrates at $U_s=U_{fl}$, $p_{N_2}=0.3$ Pa are given in Fig.1b. The temperature T_s has a strong effect on the structure of ZrCu-N film. An increase of T_s above RT results in the formation of a two phase nanocomposite film composed of Cu and ZrN characterized by clearly separated Cu(111), ZrN(111), ZrN(200) and ZrN(220) reflections. A well developed nanocomposite ZrCu-N film is produced at $T_s \geq 400$ °C. More details are given in [5].

The microhardness was measured for both ZrCu and ZrCu-N films. It was found that the microhardness of the ZrCu films (i) decreases with increasing negative bias U_s from 730 kg/mm^2 at U_{fl} to 490 kg/mm^2 at -700V and (ii) almost does not change with increasing substrate temperature T_s up to about 500 °C.

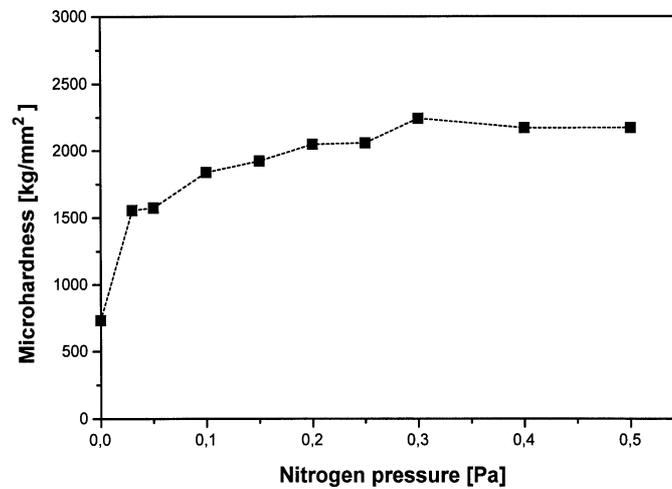


Fig. 2. The microhardness $HV_{0.001}$ of 2.3 μm thick ZrCu-N films reactively sputtered at $U_s=U_{fl}$ and $T_s=RT$ as a function of the partial pressure of nitrogen p_{N_2} .

The microhardness $HV_{0.001}$ of ZrCu-N films as a function of the partial pressure of nitrogen p_{N_2} is given in Fig. 2. The microhardness HV increases with increasing p_{N_2} from 700 kg/mm^2 at $p_{N_2}=0$ to about 2000 kg/mm^2 at $p_{N_2}=0.2$ Pa. A further increase of p_{N_2} above 0.2 Pa results in only a small increase of HV up to 2200 kg/mm^2 at $p_{N_2}=0.5$ Pa.

The microhardness of ZrCu-N films almost does not change with increasing T_s up to about 600 °C. It means that the ZrCu-N nanocomposite film composed of Cu and ZrN exhibits a good thermal stability.

4. Conclusion

A ZrCu alloy where elements are immiscible and do not form a solid solution is a good material to form easily nanocrystalline films without ion bombardment and nanocomposite films when nitrogen is added to ZrCu alloy.

Acknowledgement

This work was supported in part by the Grant Agency of the Czech Republic under Project No. 106/96/K245 and by the Ministry of Education of the Czech Republic under Project No. VS 96059 and Project No. ME 173(1998).

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