Influence of heat treatment on the structure of W-Si-N sputtered films

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Abstract. W-Si-N sputtered coatings with different chemical compositions were deposited by magnetron sputtering and annealed in $N_2(H_2)$ and $Ar(H_2)$ atmospheres up to 1400ºC. The results show that the structure of the as-deposited films depends on their chemical composition. Films with (W+Si)/N ratios close to 1 and low silicon contents are crystalline and formed by either a δ-WN or a β-W_2N structure. High silicon contents induce amorphicity of these films. This type of structure was also observed in the as-deposited films with low nitrogen contents. The $W_{46}N_{54}$ and $W_{36}Si_{15}N_{49}$ crystalline films maintain their initial structure up to temperatures of 1200ºC. The amorphous $W_{27}Si_{20}N_{53}$ coating crystallise into α-W + β-W_2N at 1050ºC. The α-W phase was detected in all the coatings with (W+Si)/N ratio close to 1 annealed at temperatures equal or higher than 1050ºC. Concerning the coatings with lower nitrogen contents ($W_{69}Si_{23}N_8$ and $W_{64}Si_9N_{27}$) annealed in an argon atmosphere the results showed that they crystallize at relatively low temperatures ($\approx$ 700ºC). Simultaneously, the films lose nitrogen. The final Si/N atomic ratio of these annealed films corresponds to the stoichiometry of the Si_3N_4 phase. The higher is the silicon content, the lower is the nitrogen loss during annealing.

Introduction

Hard coatings, mainly those deposited over cutting cools, are used in conditions where high temperature is encountered. Since thin films produced by sputtering are often metastable with either nanocrystalline or amorphous structures it is important to study their thermal stability. The annealing process induces microstuctural modifications, which are responsible for dramatic changes in mechanical properties.

Previous work on the deposition and characterisation of W-Si-N sputtered films [1-3] showed that these materials are structurally metastable and when annealed in an $Ar(H_2)$ atmosphere they have different thermal stability depending on their Si and N contents. It has been shown that nitrogen content plays an important role on the thermal stability of the amorphous structures. Moreover, during the heat treatment process, a loss of nitrogen was detected, in particular in films with low silicon percentages. This loss justifies the formation of α-W from the amorphous phase, in detriment of nitride phases, such as W_2N or WN. This paper concerns the effect of the temperature and of the annealing gas environment on the structural changes of W-Si-N coatings with different chemical compositions.

Experimental

Two sets of W-Si-N films were deposited by d.c. reactive magnetron sputtering from a W target superimposed with a different number of Si round pieces, using the aforementioned process [1]. The first set corresponds to films with 50at.% N and 0, 15 and 20at.%Si (hereby $(W,Si)_{50}N_{50}$); the second one corresponds to films depleted in nitrogen ($W_{69}Si_{23}N_8$ and $W_{64}Si_9N_{27}$). The films were deposited on NaCl substrates and detached from the substrates in distilled water.

The chemical composition of the coatings was determined by electron probe microanalysis (EPMA) using a Cameca SX-50 equipment. The annealing process was carried out in a differential scanning calorimetry (DSC) apparatus up to 1400ºC with a heating rate of 40ºC.min^{-1}. Continuous $N_2(5\%H_2)$ or $Ar(5\%H_2)$ gas flow (p=1atm) was used during the thermal runs. The structure of the films was analysed by X-ray diffraction (XRD) in a Philips X-Pert diffractometer with Co-K_{α} radiation. All the X-ray diffractograms were recorded at room temperature, after cooling in furnace from the annealing temperature.

Results and discussion

$(W,Si)_{50}N_{50}$ system

Figs. 1a), 2a) and 2b) show the results obtained from the XRD analysis performed in films with (W,Si)/N ratios ≈ 1 in the as-deposited condition and after annealing at different maximal temperatures (T_a= 950, 1050, 1200 and 1400ºC). These temperatures were selected on the basis of the peaks observed in an DSC curve obtained for the $W_{46}N_{54}$ film up to 1400ºC (Fig. 1b)).

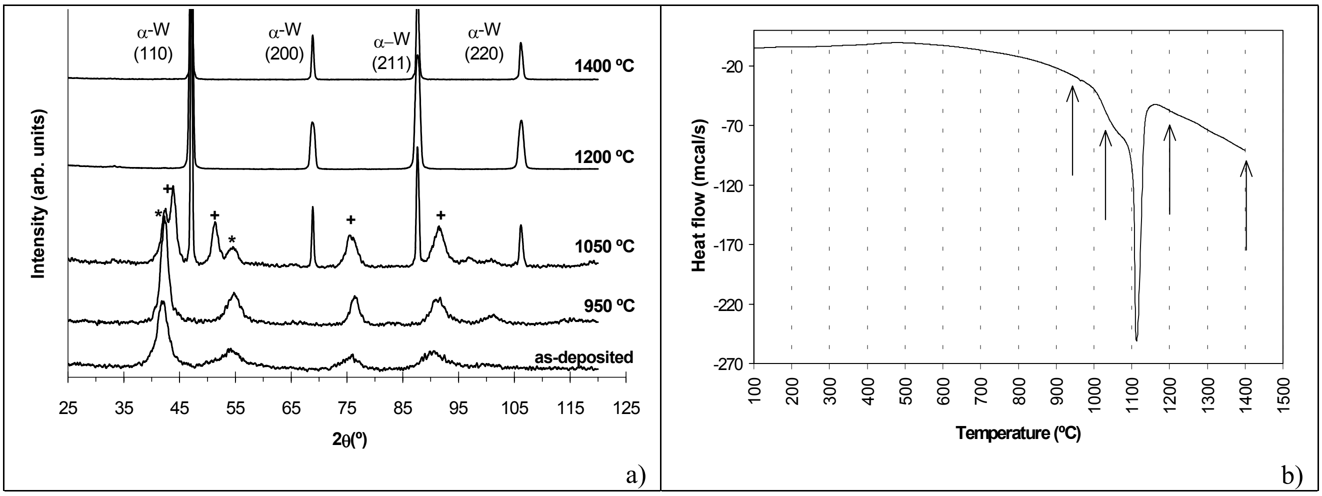

Fig. 1 - a) Structural evolution (+ = W_2N; * = WN) and b) DSC curve of $W_{46}N_{54}$ film.

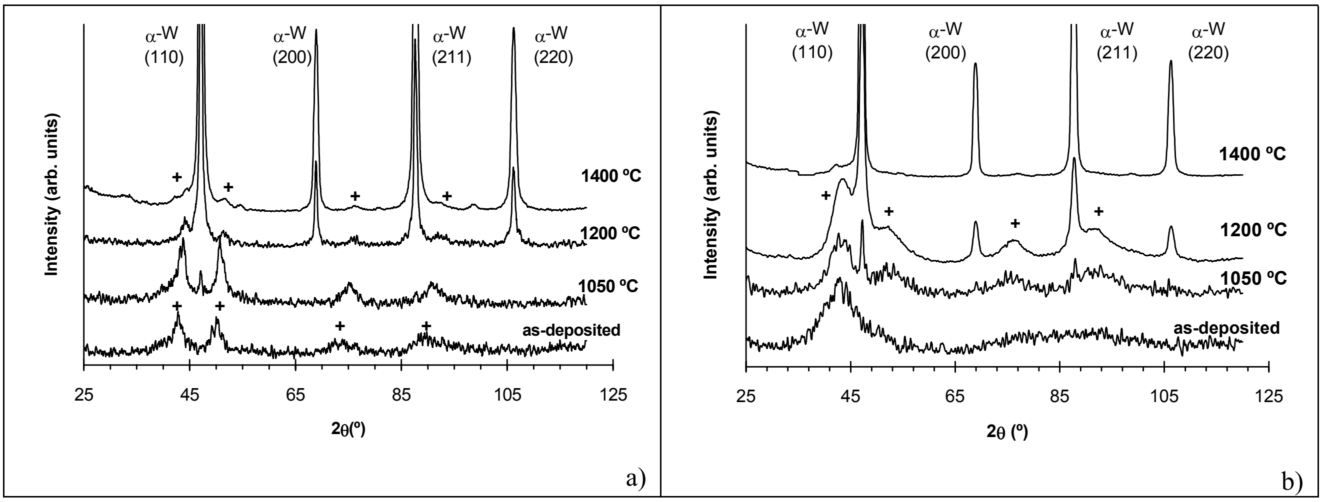

Fig. 2 - Structural evolution of a) $W_{36}Si_{15}N_{49}$ and b) $W_{27}Si_{20}N_{53}$ sputtered films with increasing annealing temperature; + = W_2N.

Concerning the structure of the films the following points can be referred:

(a) In the as-deposited condition the films present different structures. $W_{46}N_{54}$ and $W_{36}Si_{15}N_{49}$ films are crystalline whereas the $W_{27}Si_{20}N_{53}$ is amorphous. The high nitrogen content of film without silicon (54%) leads to the formation of a N-rich phase (δ-WN; ICDD 25-1256), which is confirmed by the two strong diffraction lines ((100) and (101)) corresponding to d=2.505Å and d=1.875Å. The diffraction lines of the $W_{36}Si_{15}N_{49}$ film match to the f.c.c. β-W_2N phase (ICDD 25-1257).

(b) No structural transformations were detected either in crystalline or amorphous samples up to 1050ºC. At this temperature, the formation of the b.c.c. α-W phase is detected in all the studied films. The β-W_2N phase is also clearly observed in the $W_{46}N_{54}$ film annealed at 1050ºC (Fig. 1a)). In this stage, the $W_{27}Si_{20}N_{53}$ film starts to crystallise into β-W_2N + α-W.

(c) Si plays a fundamental role in the stabilization of the β-W_2N phase. In fact, at 1200ºC, the $W_{46}N_{54}$ film does not present any vestiges of the β-W_2N phase, whereas for the other two films containing Si, this nitride phase is clearly detected, particularly in the case of the film with the highest Si content (Fig. 2b)).

(d) - In all the X-ray diffractograms of the annealed samples is still possible to observe a broad peak superimposed to the diffraction lines of both the α-W and β-W_2N phases, suggesting the presence of an amorphous phase (Fig. 3). The lack of any crystalline phase containing Si leads to the conclusion that the amorphous phase should be silicon nitride, since it is known that this phase remains amorphous up to very high temperatures [4, 5]. In this type of systems (M-Si-N, M= transition metal) the films are predicted to present a mosaic structure of M-N crystallites in a Si_3N_4 amorphous matrix [6-9].

(e) In comparison to our previous work [3] on the annealing of amorphous W-Si-N films with high Si contents, carried out in Ar(H_2) atmosphere, the results now obtained show that the losses of N are much lower if a N_2(H_2) atmosphere is used. In fact, the formation of any crystalline nitride phase was never observed during annealing in Ar(H_2), as a consequence of important nitrogen content decrease observed even for T_a<1000ºC. Moreover, it may be affirmed that nitrogen plays a decisive role on the stabilization of the amorphous phase as was observed by the increase of the crystallization temperature with increasing N content.

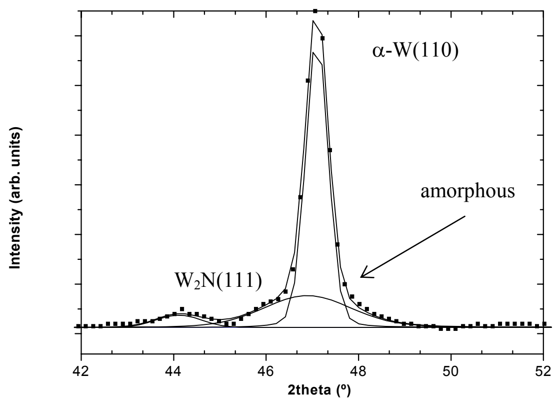

Fig. 3 – Deconvolution by curve-fitting of the XRD peaks of $W_{36}Si_{15}N_{49}$ film annealed at 1200ºC

Low N content W-Si-N films

Fig. 4 shows the x-ray diffractograms of two sputtered W-Si-N films, deposited on 310 (AISI) steel, with similar Si contents but depleted in nitrogen when compared with films of the $(W,Si)_{50}N_{50}$ system, annealed in an Ar(H_2) atmosphere. The crystallization of these films is complete for temperatures lower than 1000ºC, being registered important N losses only in the $W_{64}Si_9N_{27}$ film.

The comparison of Fig. 2a) and 2b) has shown that during the heat treatment of the $W_{36}Si_{15}N_{49}$ and $W_{27}Si_{20}N_{53}$ films in N_2(H_2) atmosphere, no-silicide phases were formed. However, in the case of the film with low nitrogen content ($W_{69}Si_{23}N_8$), W_5Si_3 is detected after 1000ºC annealing. In this case, all the nitrogen atoms might be preferentially coupled with Si, leaving the rest of Si accessible to form W-Si bonds [10] and, consequently, leading to the precipitation of the tungsten silicide phase W_5Si_3. The $W_{64}Si_9N_{27}$ film deposited on 310 (AISI) steel has a relative high percentage of nitrogen (27at.%) and consumes all Si to form a Si-N compound, impeding the formation of silicides phases. As referred to above, it is important to remark that annealing in N_2(H_2) environment does not lead to nitrogen losses from the films. Contrarily, the $W_{64}Si_9N_{27}$ film annealed in argon becomes depleted in N. Its final nitrogen content, of about 15at.%, consumes 9at.%Si in the form of Si_3N_4.

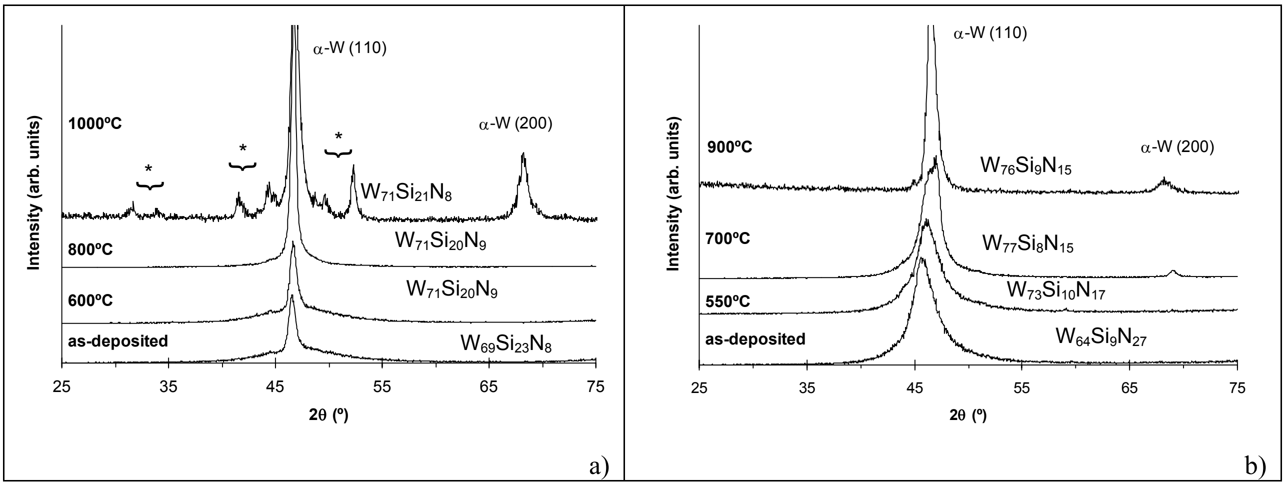

Fig. 4 – Effect of annealing temperature on the structural evolution of a) $W_{69}Si_{23}N_8$ and b) $W_{64}Si_9N_{27}$ sputtered coatings deposited on 310 (AISI) steel. * = W_5Si_3

For the Si containing films annealed in $N_2(H_2)$ the N content is enough to consume the whole Si, forming Si-N bonds (as confirmed by the presence of the amorphous phase, even for the highest annealing temperature) and to avoid the silicidation reaction. A progressive loss of nitrogen with increasing temperatures is in agreement with the increasing of α-W and decreasing β-W_2N phases amounts.

Conclusions

Films with (W+Si)/N ratio ≈1 and low silicon contents are crystalline and formed by either δ-WN or β-W_2N in the as-deposited state. High Si contents induce amorphicity of the W-Si-N films.

Films annealed in $N_2(H_2)$ atmosphere are stable up to 1050ºC, temperature for which the b.c.c. α-W was detected. The presence of Si stabilises the β-W_2N nitride as justified by its presence at temperatures of 1200ºC, inversely to what was observed for the $W_{45}N_{54}$ sputtered film. No silicides formation was observed in any of the films due to the preferential bonding of Si-N in detriment of W-Si bonding.

The films with low nitrogen contents, annealed in $Ar(H_2)$, crystallize at relatively low temperatures (≈ 700ºC). Losses of nitrogen at these temperatures occurred for the films with Si/N < ¾ (stoichiometry of the Si_3N_4 phase).

Acknowledgements

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