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Influence of titanium on the structural stability of sputter-deposited W–Co–C films

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Abstract

A film of $W_{45}Ti_9Co_{12}C_{34}$ has been synthesized by non-reactive r.f. sputtering onto a steel substrate and heat treated in a high vacuum furnace at increasing temperatures up to 800 °C. Investigation of its structure, hardness and adhesion is performed before and after each heat treatment. The results show that the presence of titanium in W–Co–C films promotes spontaneous crystallization and improves their thermal stability during annealing at increasing temperatures.

Keywords: Carbides; Coatings; Sputtering; Structural stability

1. Introduction

The high hardness and wear resistance of stable groups IVA–VIA carbide-based films made these potentially attractive as bases for industrial materials, e.g. in the production of mechanical components. Most of their practical uses imply the need to attain a degree of strain energy dissipation and toughness without detriment to hardness. Moreover, since in service transient and localized temperatures may eventually occur, another requirement is a good thermal stability.

In previous studies on sputtered W–(Co, Fe)–C [1] and W–Ni–C [2] films we showed that the addition of a group VIIIA transition metal to W–C films induces amorphization of the structure. Moreover, these films are not stable at high temperatures; when heat treated, they lose carbon into the steel substrates, tending to reach equilibrium by giving rise to multiphase materials formed by MC, M_2C and/or M_6C, depending on the composition. It was suggested that partial replacement of one of these group VIIIA metals by an element with higher affinity to carbon (e.g. titanium) should improve the stability of the (W–C)-based films at high temperatures.

The present study reports the characterization of a sputter-deposited $W_{45}Ti_9Co_{12}C_{34}$ film and its annealing behaviour at increasing temperature. Investigation of the structure-mechanical property relationship of this coating is presented before and after heat treatment. The results will be compared with those obtained for similar coatings without titanium [1,3].

2. Experimental details

2.1. Materials

A sintered WC–10at.%Co target partially covered by a titanium foil was used. High speed steel M2 (AISI) heat treated (quenched and tempered) with a hardness of 8.50 GPa was utilized as the substrate. The substrates were polished with diamond paste of particle size down to 0.25 μm.

2.2. Deposition technique

The films (4 μm thick) were deposited in an ESM 100 Edwards sputtering apparatus, with a deposition rate of 0.3 nm s^{-1} and an argon pressure of 1 Pa. Prior to the depositions, the substrates were sputter cleaned at −1000 V for 5 min in an argon atmosphere.

2.3. Characterization techniques

After characterization of the as-deposited state, the thin films were annealed in a high vacuum furnace (10^{-5} Pa) at increasing temperatures. Owing to the ferrite→austenite transformation of the steel the highest annealing temperature attained in this work was 800 °C.

The chemical composition of the films was determined by electron probe microanalysis with CAMECA SX50 equipment. Microstructural characterization was performed by X-ray diffraction (XRD) (INEL apparatus) using Co Kα radiation, and transmission electron microscopy (TEM) (JEOL 200CX microscope). The hardness values were obtained using a Shimadzu microhardness indenter under a load of 0.25 N. Each hardness value presented is an average of ten measurements carried out with a dwell time of 15 s. The scratch tests were performed using commercial scratch testing equipment (CSEM Revestest) fitted with an acoustic detector. The morphologies of the scratch channels were observed by means of an optical microscope (Nikon HFX-II) and a scanning electron microscope (JEOL JSM-T330). The latter was fitted with an energy-dispersive X-ray analyser (TRACOR), permitting locus-of-failure identification.

3. Results and discussion

3.1. As-deposited state

The results of the chemical and structural analyses of the as-deposited $W_{45}Ti_9Co_{12}C_{34}$ film are summarized in Table 1 and Fig. 1 respectively.

The chemical composition of the W–Ti–Co–C film deviates slightly from that of the target, with a W-to-C ratio higher than the unity. The depletion in carbon of the (W–C)-based films obtained by sputtering from sintered materials has been interpreted in terms of the different sputtering yields for the elements of the targets [1]. Despite the lower elemental sputtering yield of carbon relative to cobalt and tungsten [4] (for ion bombardment energies up to 1000 eV) for multicomponent materials a tendency for the lightest species (carbon in the present work) to sputter preferentially has been predicted [5–6]. The film bombardment that occurs during the sputtering process leads to W–Ti–Co–C films richer in metal and deficient in carbon.

Table 1
Atomic chemical composition of the as-deposited $W_{45}Ti_9Co_{12}C_{34}$ film

Film designation	Analysed composition (at.%)					
	W	Ti	Co	C	O	Ar
$W_{45}Ti_9Co_{12}C_{34}$	43.5	6.9	10.2	33.3	4.5	1.6

The as-deposited $W_{45}Ti_9Co_{12}C_{34}$ film is characterized by an extremely fine-grained structure of β-MC_{1-x} [7] (Fig. 1). This carbide is a high temperature phase with an NaCl-type structure [8]. The occurrence of β-MC_{1-x} at room temperature in sputtered M–C (M = metal from groups IVA–VIA) seems to be the result of the substantially high quench rate inherent in the sputtering method and the wide range of compositions of the β-MC_{1-x} structure ($0<x<0.5$) [9]. The results of structural analysis show that the effect of adding titanium solute atoms to a W–Co–C amorphous system is to require that spontaneous crystallization occurs during the formation of the film. The reason why the as-deposited $W_{45}Ti_9Co_{12}C_{34}$ film is crystalline, whilst the $W_{50}Co_{13}C_{37}$ film [1] is amorphous may be explained by the model of cohesion of TiC_{1-x} and related compounds proposed by Cottrell [9]. According to this author, the strong cohesion of these transition metal carbides is mostly due to strong covalent bonds between the p electrons of the non-metal atom and the d electrons of the transition metal (one in the s band, two in the pd(σ) bonding orbitals, and one in the pd(π) bonding orbitals). In other words, each carbon atom always claims four electrons from its titanium neighbours, forming "saturated bonds" with them. According to this model, substitution of a group IVA element by a later transition metal (more d electrons) enables more dd(σ) bonding orbitals to fill metal–metal nearest neighbours. This induces weakening of the metal–carbon covalent bonds and strengthening of the metal–metal bonds. The contribution of these to the cohesion of the carbide is less important than the former. Conversely, the addition of titanium to the W–Co–C system gives rise to a greater number of metal–carbon strong bonds and promotes the growth of the β-MC_{1-x} crystallites.

Fig. 2 shows a cross-sectional scanning electron micrograph of the as-deposited $W_{45}Ti_9Co_{12}C_{34}$ film. Its morphology is featureless with no apparent porosity or

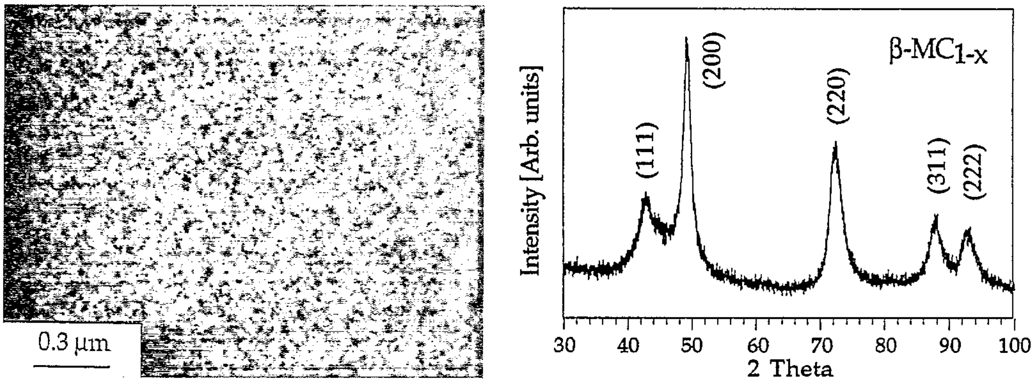

Fig. 1. Structure of the as-deposited $W_{45}Ti_9Co_{12}C_{34}$ film: left, TEM; right, XRD.

Fig. 2. Cross-sectional scanning electron micrograph of the as-deposited $W_{45}Ti_9Co_{12}C_{34}$ film.

microcraking. The scratch track micrographs are shown in Fig. 3. The failure of the film occurs cohesively without presenting spalling. The tensile cracking appears in the track before conformal cracking. To the first cohesive failure corresponds a critical load $L_{c1}=18$ N. This value is slightly higher than those reported for W–Co–C films obtained with similar deposition conditions (10–15 N depending on the cobalt content [3]). The hardness of the film in the as-deposited condition is 20.80 GPa, which does not differ from the value indicated by Cavaleiro and Vieira [3] for a similar W–Co–C film without titanium.

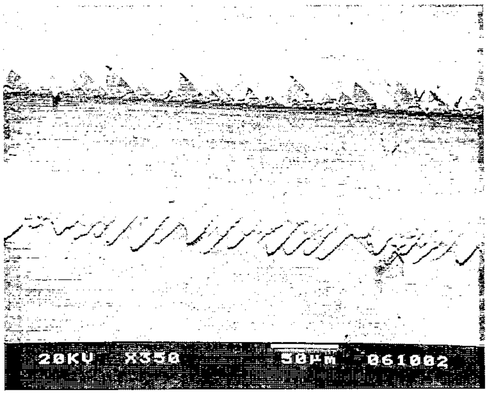

Fig. 3. Scratch track micrograph of the $W_{45}Ti_9Co_{12}C_{34}$ film.

3.2. Annealing behaviour

No microstructural changes were observed during the successive isothermal annealings of the $W_{45}Ti_9Co_{12}C_{34}$ film up to 800 °C. Only at this temperature did the β-MC_{1-x} start to decompose, giving rise to $MC+M_2C$ (Fig. 4). Conversely, the amorphous as-deposited W–Co–C films without titanium crystallize at lower temperatures ($T \leqslant 700$ °C), giving rise to multiphase materials formed by MC, M_2C and/or M_6C depending on the composition [1] (Fig. 5). This confirms that titanium stabilizes the crystalline β-MC_{1-x} structure.

In spite of the thermal stability of the β-MC_{1-x} phase, carbon depletion of the films is observed for annealing temperatures equal to or higher than 700 °C (Fig. 6). This depletion is due to the carbon diffusion from the $W_{45}Ti_9Co_{12}C_{34}$ film into the steel substrate, as already observed for W–(Co, Fe)–C [1] and W–Ni–C [2] films.

The present work reveals that the carbon atom migration precedes beginning of the as-deposited phase structural transformation (β-MC_{1-x} phase in this case). If it is taken into account that the atomic percentage of carbon of the as-deposited film ($MC_{0.52}$) is very close to the lower limit of carbon indicated for this carbide ($MC_{0.5}$), a small decrease in its carbon-to-metal ratio is enough to induce the transformation β-$MC_{1-x} \rightarrow MC+M_2C$.

Concerning the mechanical properties, the critical load was found to be interrelated with hardness. Fig. 7 shows the dependences of L_{c1} and Vickers hardness on the annealing temperature. Both curves show an increase up to 500 °C, followed by a sudden decrease at higher temperatures.

Since no changes in structure and chemical composition were observed at the first annealing stages, the increase in both L_{c1} and hardness values at annealing temperatures lower than 550 °C ("secondary hardening" temperature of the M2 steel) may be explained by the following effects: (i) fine precipitation of a structural phase (MC eventually) from β-MC_{1-x} not detectable by XRD and (ii) stresses induced by the heat treatment as

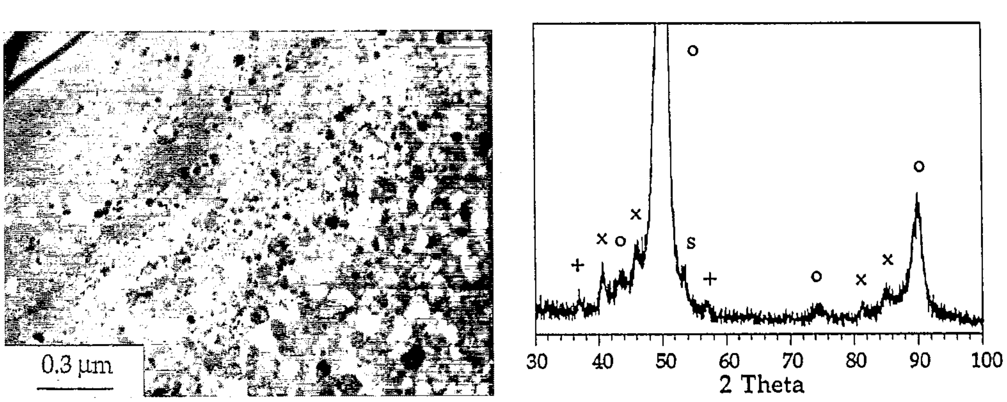

Fig. 4. Structure of the $W_{45}Ti_9Co_{12}C_{34}$ film after annealing for 1 h at 800 °C. o, β-MC_{1-x}; s, Fe-α (substrate); ×, M_2C; +, MC: left, TEM; right, XRD.

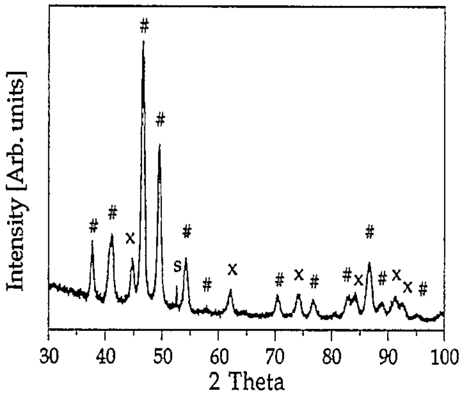

Fig. 5. XRD pattern obtained in previous work [1] from the $W_{50}Co_{13}C_{37}$ film annealed for 1 h at 750 °C: s, Fe-α (substrate); ×, M_2C; #, M_6C.

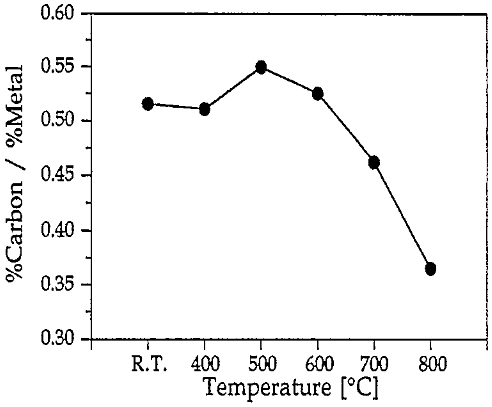

Fig. 6. Carbon-to-metal atomic ratio of the $W_{45}Ti_9Co_{12}C_{34}$ film at room temperature (R.T.) and after annealing at increasing temperature.

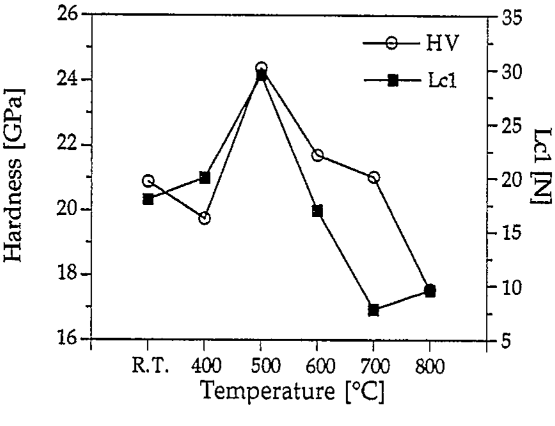

Fig. 7. Vickers hardness (HV) and adhesion of the $W_{45}Ti_9Co_{12}C_{34}$ film at room temperature (R.T.) and after annealing at increasing temperature.

the result of the different thermal expansion coefficient values of both the film and the substrate materials (see for instance [10]). With increasing annealing temperature, softening of the substrate and carbon impoverishment of the films occur, which cause deterioration in the mechanical properties of the film–substrate component.

4. Conclusions

The results show that the addition of titanium to amorphous W–Co–C films promotes spontaneous crystallization during their formation. Moreover, it improves thermal stability at high temperatures by the stabilization of the β-MC_{1-x} phase. The crystalline $W_{45}Ti_9Co_{12}C_{34}$ film constitutes a potentially interesting hard coating for mechanical applications requiring a good thermal stability of the coating–substrate component.

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References

[1] B. Trindade, M.T. Vieira and E. Bauer-Grosse, *Mater. Sci. Eng., A174* (1994) 165.
[2] B. Trindade, M.T. Vieira and E. Bauer-Grosse, *Thin Solid Films*, 252 (1994) 82.
[3] A. Cavaleiro and M.T. Vieira, *Mater. Sci. Eng., A140* (1991) 631.
[4] R.V. Stuart and G.K. Wehner, *J. Appl. Phys., 33* (1962) 2345.
[5] P. Sigmund, *Sputtering by Particle Bombardment, Top. Appl. Phys.*, (1981) 10.
[6] H.F. Winters, *J. Vac. Sci. Technol., 3* (1982) 493.
[7] Joint Committee on Powder Diffraction, *Powder Diffraction File*, International Center for Powder Diffraction Data, Swarthmore, PA, 1967 Card 20-1316.
[8] G.V. Raynor and V.G. Rivlin, *Phase Equilibria in Iron Ternary Alloys*, Institute of Metals, London, 1988, p. 25.
[9] A.H. Cottrell, *Mater. Sci. Technol., 10* (1994) 22.
[10] N.A. Waterman and M.F. Ashby (eds), *Elsevier Materials Selector*, Vol. 1, Elsevier, London, 1991, p. 183.