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N.B.: When citing this work, cite the original article.

Original Publication:

Andrej Furlan, Jun Lu, Lars Hultman and Ulf Jonsson, Control of crystallinity in sputtered Cr–Ti–C films, 2013, Acta Materialia, (61), 17, 6352-6361.

<http://dx.doi.org/10.1016/j.actamat.2013.06.045>

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Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-99400>

Control of crystallinity in sputtered Cr-Ti-C films

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Abstract

The influence of Ti content on crystallinity and bonding of Cr-Ti-C thin films deposited by magnetron sputtering have been studied by X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy, and Raman spectroscopy. Our results show that binary Cr-C films without Ti exhibit an amorphous structure with two non-crystalline components; amorphous CrC_x and amorphous C (a-C). The addition of 10-20 at% Ti leads to a crystallization of the amorphous CrC_x and the formation of a metastable cubic $(\text{Cr}_{1-x}\text{Ti}_x)\text{C}_y$ phase. The observation was explained based on the tendency for formation of crystalline carbide films among the 3d transition metals. The mechanical properties of the films determined by nanoindentation and microindentation were found to be strongly dependent on the film composition in terms of hardness, elasticity modulus, H/E ratio, and crack development.

Keywords: Carbides; Thin films; Crystallization; Amorphous alloy; Sputtering

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1. Introduction

Magnetron sputtering can be used to produce amorphous thin films. This can be explained by the fact that the sputtering process is carried out at kinetically-limited conditions, where the impinging atoms are subject to quenching rates above 10^6 K/s, which is well above the rates required when metallic glasses are formed from melts [1]. Amorphous films have many applications, but a major problem is their susceptibility for brittle-crack propagation, which may limit their applicability in mechanically demanding environments [2,3]. This problem can potentially be reduced by the controlled addition of a nanocrystalline component forming a nanocomposite. The crystalline grain boundaries may then act as a hinder to crack propagation, leading to an increase in fracture toughness of the amorphous/nanocrystalline nanocomposite structure compared to the pure amorphous coating.

A potentially interesting group of amorphous thin films is transition metal carbides that exhibit, e.g., a combination of high corrosion resistance and specific magnetic and mechanical properties. A survey of the literature shows some general trends for sputtered metal carbides. Typically, the group IV metals Ti, Zr, and Hf form crystalline films although the carbide often is present as nano-sized crystallites in an amorphous carbon (a-C) matrix, depending of the C content. The properties of these nanocomposites are typically affected by the relative amount of a hard carbide phase in a softer a-C matrix [4-7]. For the 3d transition metals, the tendency to form amorphous films increases with increasing number of d-electrons in the metal and sputtered Cr-C and Fe-C films are therefore often amorphous [8-11]. This trend has been explained based on factors such as differences in atomic radii, carbide stability, and carbide crystal structure (see, e.g., ref. [1,12]). The importance of crystal structure can be illustrated by the group IV metals including Ti, which form simple cubic B1-type structure (NaCl) carbides while the later transition metals

form complex structures such as cubic Cr_{23}C_6 . The more complex carbide structures have rather large lattice constants and require extensive diffusion to form. Furthermore, they mix carbon in both octahedral and prismatic sites, which is seen to favor amorphous growth [8,12,13]. Andersson et al. have recently studied magnetron sputtering of chromium carbide films and observed a difference between reactive sputtering and sputtering from elemental targets [4]. A general observation is that elemental targets favor a completely amorphous growth, while a reactive process also can yield nanocrystalline carbide grains in an amorphous matrix.

Crystallization of an amorphous carbide film can be obtained by changing the growth conditions during sputtering. For example, Ziebert et al. have demonstrated that an increase in the ion flux during growth can lead to a change in growth mode from amorphous to nanocrystalline chromium carbide films [14]. An alternative approach can be to add a crystallization agent to reduce the tendency to form amorphous structures and, in principle, make it possible to control also the degree of crystallization. The aim of this work is to use this approach and add Ti as a crystallization agent for chromium carbide films. Ti has been selected based on the general trend in formation of crystalline structure by group IV metals, as described above, as well as for its wider availability with respect to other for the purpose adequate metals. Furthermore, Ti has previously been used as dopant to steer crystallization of amorphous Cr-C carbides in the bulk form [15,16]. Here, we investigate the phase composition as a function of Ti content for two series of $\text{Cr}_{1-x}\text{Ti}_x\text{C}_y$ films with different carbon contents. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy are used to study structure and chemical bonding in the films. We also examine the mechanical properties, including hardness, plastic deformation, and crack propagation, for the films as a function of Ti content and structure.

2. Experimental

The Cr-Ti-C films were deposited by nonreactive dc sputtering in an ultra high vacuum (UHV) chamber with a base pressure of 10^{-9} Pa from triple current-regulated 2-inch magnetrons in pure Ar discharge generated at 3.0 mTorr and with gas flow rate of 30 sccm. The magnetrons were directed towards a rotating substrate holder at a distance of 15 cm. As sputtering sources, elemental targets of graphite (99.999 %), Cr (99.95 %), and Ti (99.95 %) were used. Control of the film composition was achieved by keeping the graphite target at the constant current of 300 mA and tuning the current on the Cr and Ti targets. The Cr and Ti targets were calibrated by thickness measurement of pure metal films using X-ray reflectivity (XRR). The substrates were biased to -50 V or kept at the floating potential determined to -9 V for three magnetrons running and preheated to around 250 °C from the back side by a resistive heater in the substrate holder. The thicknesses of as-deposited coatings were 0.64 μm – 1.1 μm , giving a deposition rate of 2.6 – 4.2 nm/min, depending on the amount of carbon in the films. Single-crystal Si(001) (10 x 10 mm) wafers were used for film thickness, structural, and compositional analysis, and Al₂O₃ (10 x 10 mm) wafers for studies of the mechanical properties.

The structural properties of thin films were determined by XRD. In order to avoid diffraction signal from the Si substrate a grazing incidence (GI) XRD measurements were carried out on a Siemens D5000 using Cu K α radiation source operated at 45 kV and 40 mA and parallel beam geometry with a 2° incidence angle. The chemical composition of the films was determined by XPS using a Physical Systems Quantum 2000 spectrometer with monochromatic Al K α radiation. Energy calibration was carried out with Au and Ag reference samples and the sensitivity factors used for quantitative analysis were determined by elastic recoil detection analysis (ERDA) of reference samples. Depth profiles of the films were acquired by rastered Ar⁺-ion sputter etching over an area of 2 x 2 mm² with ions being accelerated by the potential difference of 4 kV. High resolution scans of the selected peaks were acquired after 45 min, 30 min or 6 min of Ar⁺-ion sputter etching with ions being accelerated by the potential difference of 200 V, 500 V or 4 kV, respectively, to evaluate sputter-induced damages. The XPS analysis area was set to a diameter of

200 μm in all measurements. To confirm the elemental composition of selected coatings time-of-flight energy elastic recoil detection analysis (ToF-E ERDA) was performed at the Uppsala Tandem Laboratory. We used 40 MeV $^{127}\text{I}^{9+}$ projectile ions at 22.5° incident angle and a detector placed at a recoil scattering angle of 45° [17]. In order to correlate the nanostructuring and sp^2/sp^3 ratio of the films to Ti concentration, Raman scattering spectroscopy was performed on the samples at room temperature in the range 800-1900 cm^{-1} in the back-scattering configuration using UV 325 nm laser excitation. Scanning electron microscopy (SEM) was performed in a LEO 1550 microscope. Cross-sectional and plan-view images were obtained by using accelerating voltages of 20 kV and 15 kV, respectively, in secondary electron imaging mode.

Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and scanning TEM (STEM) images were obtained in a Tecnai G² 20 U-Twin 200 kV FEGTEM. Analytical TEM was performed using energy-dispersive x-ray spectroscopy (EDX) in STEM mode. Cross-section samples were mechanically polished, and ion milled to electron transparency by a Gatan Precision Ion Polishing System (PIPS). Hardness and elastic modulus of the films were determined by the Oliver-Pharr [18] method using a CSM Instruments nano-indenter XP with a diamond Berkovich tip. All nanoindentation tests were performed for the tip penetration depth of around 10% of the film thickness. Fracture propagation was studied by Rockwell analysis of indents done by microindentation with a Berkovich tip loaded by 100 g.

3. Results

The properties of transition metal carbide films are known to be strongly affected by the presence of amorphous carbon (a-C). For this reason, two series of $(\text{Cr}_{1-x}\text{Ti}_x)\text{C}_y$ films were synthesized with different C contents. Figure 1 shows the sample compositions obtained by XPS analysis. The low carbon content (LC) series contains 32.2 ± 3.6 at.% of C, and the high-carbon content (HC) series contains 46.5 ± 3.8 at.% of C.

Fig. 2 shows XRD diffractograms for both the a) LC and b) HC series as a function of Ti content x . As can be seen, the pure chromium carbide films ($x=0$) are X-ray amorphous in both series, while the pure titanium carbide films ($x=1$) are clearly crystalline. It is thus obvious that the addition of Ti into the chromium carbide leads to crystallization. In the LC series, the $(\text{Cr}_{1-x}\text{Ti}_x)\text{C}_y$ films show crystalline peaks starting at $x=0.28$, while diffraction peaks are observed already at $x=0.16$ in the HC series. All peaks can be assigned to a cubic B1 structure similar to TiC. Another observation for both HC and LC series is that the peaks are shifted up in diffraction angle with increasing Ti content. An almost linear dependence of a lattice constant with x was observed for the HC series (see Fig. 3). As discussed below the corresponding reduction in cell parameter with increased Cr content can be explained by a substitutional solid solution of Cr on the metal sites in the cubic TiC structure.

A closer inspection of Fig. 2 shows that the diffraction peaks are very broad, which can be attributed to a small grain size of the carbide. The sizes of the crystallites were determined to 3-5 nm for most Cr-containing films using the Scherrer equation (all peaks included in the calculation). In contrast, the pure Ti-C films ($x=1$) and the film with $x=0.7$ in the HC series exhibit much sharper peaks corresponding to grain sizes of 170-250 nm.

Fig. 4 shows TEM micrographs with corresponding SAED patterns from representative samples of the LC series. The most carbon-rich film with $x=0.1$ is clearly amorphous as shown of Fig. 4a, and displays a columnar structure (Fig. 4a, inset I). The diameter of the columns is 10 nm. An interesting feature is that in the structure near the interface the columns are no longer visible (not shown). The film with $x=0.28$ is partly crystalline and the crystallites have a diameter of ~ 2 nm (Fig. 4b). This film also exhibits a small 002 texture. Some amorphous regions can be observed, but no significant amounts of C-rich matrix can be identified. For $x=0.1$, the structural characteristics of both films observed by TEM is in accordance with our XRD results, which showed an amorphous structure, while for $x=0.28$ the films are at least partially crystalline. Fig. 4c shows the TEM micrograph of the film with $x=0.71$. This film has a strong

100 texture, especially near the surface region, but a clear 111 texture is detected at the substrate/film interface. Fig 4d shows the micrograph for the pure TiC film ($x=1$), which is polycrystalline.

Fig. 5 shows SEM cross-sections of the LC films for $x=0.10$, 0.28, 0.71, and 1.0. For the low Ti content film ($x=0.1$), SEM shows conformal results to the TEM analysis with a columnar structure and a glass-like fracture of the cross-section. Interestingly, films with $x=0.28$ and $x=0.71$ (Fig. 4b and c) display much less pronounced columnar structure. The pure TiC film (Fig. 5d) has both columnar structure and uneven cross-section surface typical for crystalline materials. For the HC films, the columnar structure was much more pronounced in films with high Ti content films (not shown).

Fig. 6a and 6b show XPS C1s peaks from both LC and HC films, respectively. There are two clear peaks within the displayed binding energy range; a low energy component peak in the region 281.6 eV to 283.1 eV corresponding to the C-Me bonds, and a high-energy peak between 284.3 eV and about 285.1 eV originating from C-C bonds. Obviously, the relative intensity and the position of both peaks are dependent on the Ti content. The pure Cr-C films ($x=0$) have a carbide peak at 283.1 eV, which corresponds to C-Cr bonds. As Ti is alloyed into the films, this peak shifts towards lower binding energies reaching 281.6 or 281.9 eV for the pure Ti-C films, which is in agreement with the literature data for C-Ti [19]. The shift is close to linear with the Ti content (see inset in Fig. 6b) and reflects a continuous exchange of Cr to Ti in the carbide structure.

Also the C-C peak is affected by the Ti content (see inset in Fig. 6a). The LC films are metal-rich and the films with low Ti contents exhibit only a weak C-C peak at ~ 284.7 eV. Peak fitting suggests that the total area of the C-C peak corresponds to $\sim 20\%$ of the total C1s peak area in the pure Cr-C film. The relative intensity of the C-C peak increases strongly at $x=0.28$. It is interesting to note that this composition agrees with the change from amorphous to crystalline structure observed in the XRD diffractograms in Fig. 2. Also, the increase in amount of C-C at $x=0.28$ is followed by a small peak shift towards higher binding energies. As the Ti content in the LC series is increased, the relative amount of C-C is further reduced and

the peak position is shifted back towards lower binding energies. For the more carbon-rich series, HC, in Fig. 6b, a similar behavior can be observed. In this case, the pure Cr-C film contains much more free carbon (C-C). Peak fitting shows that as much as 45% of the carbon in this film is bonded as C-C leaving 55% to C-Cr. As the Ti content in the HC series increases, more C-C is initially formed at $x=0.15$ where crystallization starts followed by a reduced amount of C-C towards $x=1$.

Raman spectroscopy was carried out on a selected number of samples. While the signal was too weak to identify any clear peaks in the LC films, spectra from the HC series exhibited two peaks at about 1410 and 1580 cm^{-1} typical for D and G peaks in amorphous carbon (not shown). The spectra was almost identical to those in ref.[4] and no clear influence of Ti on the $I(D)/I(G)$ ratios, which are related to the sp^2/sp^3 bonding ratio, could be observed.

The hardness and elastic moduli of all films obtained by the O-P method are summarized in Figs. 7a and 7b, respectively. Comparing the two Cr-C films ($x=0$) of the LC and HC series, we can see that C-rich films are less hard and also has a lower modulus of elasticity than the corresponding C-poor films. The addition of Ti clearly affects both hardness and elasticity. In the LC series, the hardness initially decreases slightly followed by a significant hardening with larger amount of Ti. For the HC series, however, the film hardness initially increases followed by a reduction in hardness with increasing Ti content. The elastic modulus shows similar trends. In the HC series, the modulus is initially slightly reduced and levels out for higher Ti contents with the exception of the film at $x=0.71$, which shows a substantially higher value for the elastic modulus. In the LC series, the addition of Ti increases the elastic modulus. The pure TiC film ($x=1$) has a similar modulus of elasticity as the more Cr-rich films. Also in this case, the film at $x=0.7$ shows a deviating value for the elastic modulus, but in the opposite direction compared to corresponding LC film. The H/E ratios for all films are summarized in Fig. 8. As can be seen this ratio increases more or less linearly from about 0.05 to 0.08 for LC. A similar behavior was observed for the HC films with the exception for the pure Ti-C film, where the H/E ratio dropped significantly to ~ 0.045 .

An interesting question is how the crystallinity affects the plastic deformation of the films. The inset in Fig. 7 shows load-unload curves for two representative films of the LC series. The amorphous film with $x=0.1$ has a strong permanent deformation after unloading (low elasticity). In comparison, the crystallized film with $x=0.71$ exhibits much less permanent deformation. This trend is also confirmed by Rockwell microindentations performed on the same films. Fig. 9 shows microindents on six representative LC films. It is clear that the pure Cr-C film (Fig. 9a) exhibits a substantial pile-up at the edges of the indent due to the plastic deformation. For the film with $x=0.44$ (Fig. 9d), there is less pronounced pile-up and the effect disappears completely for films with $x=0.71$ (Fig. 9e) and pure Ti-C (Fig. 9f). Microindentation of the C-rich films shows that the plastic deformation pile-up is not present for any of the examined films (Fig 10). The pure Cr-C film (Fig 10a) shows, however, the largest residual indent compared to the other three shown films (Fig 10b, c, d). This suggests a more pronounced susceptibility to plastic deformation of the pure Cr-C film compared to films containing Ti.

In connection to the plastic deformation dependence on x , we examined more closely the crack development in the films. Fig. 9 shows that the microindentations induced the most pronounced crack propagation in $(\text{Cr}_{1-x}\text{Ti}_x)\text{C}_y$ films with high Ti contents (Figs. 9d and 9e). Interestingly, the pure TiC (Fig. 9f) displays no visible cracks. No or few cracks were detected in the mainly amorphous films (Figs. 9a, b, c). For the carbon-rich HC films (see Fig. 10), cracks are present around the indents in all films.

4. Discussion

Our results show that Ti act as a crystallization agent in amorphous Cr-C films giving a nanocomposite structure of nc- $(\text{Cr}_{1-x}\text{Ti}_x)\text{C}_y$ and amorphous C. This agrees with reports in [15] and [16]. The presence of the amorphous carbon component is shown here by both XPS and Raman spectroscopy. The results from the LC series actually show that some Cr remain in an amorphous state, although it has not been possible to attain a complete control of microstructure of two carbide components.

Both Cr-C films in the LC and HC series ($x=0$) are amorphous and have a mixture of C-Cr and C-C bonds. Recently, Magnuson et al. [20] and Andersson et al. [4] have demonstrated that sputtered non-crystalline Cr-C films can consist of two amorphous components: amorphous CrC_x and amorphous C (a-C). Also the pure Cr-C films in our study can be described as a mixture of two non-crystalline phases. The composition of the carbidic component in the two binary Cr-C films in our study can be determined by subtracting the C-C peaks in the C1s XPS spectra and calculate the amount of carbon in the carbidic phase. This calculation shows that the amorphous carbidic phase contains about 30 at % C for both Cr-C films ($x=0$). This is close to the composition of the crystalline carbide Cr_7C_3 and in agreement with results in refs. [4,20].

The addition of Ti clearly induces a crystallization of the amorphous structure. As stated in the introduction this can be predicted from general trends among the 3-d transition metals discussed by, e.g., Bauer-Grosse where Ti generally forms crystalline films while amorphous films easily are formed for metals with more d-electrons [9]. Our results also show that the carbon content influences the critical concentration of Ti required for crystallization. The films in the carbon-rich HC series crystallize at a lower Ti content than the more metal-rich films in the LC series. Similar crystallization rate dependence on C content has been recently reported for $\text{Cr}_{1-x}\text{C}_x$ films by Magnuson et al. [20]. They demonstrated that films with a composition of around 45 at% C crystallize more easily than films with either lower C content, such as 25 at%, or higher including 67 at% and 85 at% of C. The reason for such crystallization behavior should be looked for at the film composition that with the ~45 at% of C lies near the composition for the stoichiometric cubic Cr-C with NaCl structure that crystallizes easily due to less diffusivity required to build a crystalline structure.

The carbide phase observed in the diffractograms is the cubic B1-type (NaCl) normally formed in Ti-C. This structure is not thermodynamically stable for pure Cr-C or for Cr-rich solid solutions with Ti-C. The maximum solid solubility of Cr in TiC at equilibrium has been studied by several authors, see e.g., [15,21,23]. Guha and Kolar have determined the maximum solubility at 1100 °C to be less than about 4

at% [15]. Other studies, however, indicate a higher solid solubility ranging from 10 at% to 25 at% at temperatures above 1300 °C [21, 23]. The solid solubility decreases usually with temperature and it is therefore conceivable that the solubility at room temperature is less than observed in refs. [15, 21-23]. This limited solid solubility can be explained by considering the density-of-states (DOS) for cubic Ti-C [24,25]. With Ti all bonding states are occupied giving a Fermi level just below the non-bonding/antibonding states. Solution of other transition metals with more d-electrons on the Ti sites such as Cr would add extra electrons into the non-bonding/antibonding states and destabilize the structure [20]. This can partly be handled by reduced carbon content (i.e. carbon vacancy formation), but imposes a strong limitation on solid solubility of many transition metals.

Fig. 3 shows that the lattice constant for the pure Ti-C ($x=1$) is 4.327 Å for the LC series and 4.34 Å for the HC series. These values are close to previously published theoretically calculated data [26]. Furthermore, the determined small variation of the lattice parameter for the two C contents shows that the C content does not influence the lattice parameter. This is further supported by the observation that the lattice parameter in TiC_y changes less than 0.5 % going from $\text{TiC}_{0.6}$ to $\text{TiC}_{0.4}$ [32]. As the Ti content decreases, the lattice constant is reduced. This can be explained by a solid solution of the smaller Cr atoms on the Ti sites in the cubic structure thus forming a metastable $(\text{Cr}_{1-x}\text{Ti}_x)\text{C}_y$ phase. For the HC series, all lattice parameter values lie near the line connecting literature data for the lattice of the pure TiC_y and CrC_y ($x=0$) phase. The later determined by Bewilogua et al. for ion plated cubic Cr-C to 4.1 Å [28]. That means that the HC series films follow Vegard's law with a linear correlation between lattice constant and composition even if there is an amorphous part in the pure CrC and low Ti content $(\text{Cr}_{1-x}\text{Ti}_x)\text{C}_y$ films. This indicates that most of Cr in the film in the HC series is incorporated in the metastable $(\text{Cr}_{1-x}\text{Ti}_x)\text{C}_y$ phase. In contrast, some of the more Cr-rich films in the LC series have a lattice constant above the line connecting pure TiC (4.32 Å) and CrC (4.1 Å), indicating that some of the Cr in the film is, due to the lower C content, not included into the crystalline carbide phase, but is left in an amorphous state. It should be noted, however, that Singh et al. observed a slightly smaller cell axis of 4.04 Å for

cubic CrC formed in Cr-doped diamond-like carbon films (DLC) [29]. This lattice constant would give a larger slope of the line in Fig. 3 and imply that more Cr is in the amorphous state.

The results discussed above suggest that most of the metal in the crystallized carbon rich HC series films form a metastable cubic $(\text{Cr}_{1-x}\text{Ti}_x)\text{C}_y$ phase. It is then possible to estimate the carbon content, y , in this phase by determining the amount of carbidic carbon from the C1s XPS spectra (can be directly calculated from Fig. 6 assuming that the amount of carbidic carbon and C-C add up to 100%) and divide this value with the total concentration of Ti and Cr (assuming that all metal is included in the carbide). For the most Cr-rich film in the LC series ($x=0.15$), such a calculation gives a total composition of $\text{Cr}_{0.85}\text{Ti}_{0.15}\text{C}_{0.4}$ while the pure Ti-C ($x=1$) has a composition of $\text{TiC}_{0.6}$. Variation of y dependent of x is observed for all C contents. A calculation for the LC series gives the similar trend, but the values are not reliable due to presence of Cr in the remaining amorphous component. The rather low carbon content in the carbide is due to carbon vacancies in the structure, but is clearly within the homogeneity range for the cubic TiC phase [30].

An interesting observation is that the amount of carbon in the carbide is reduced at high Cr contents. This is in agreement with the inset in Fig. 5a showing an increase in the amount of C-C directly after crystallization followed by a subsequent decrease at higher Ti concentrations. This behavior is also expected based on the fact that carbon vacancies would decrease the number of electrons in antibonding states in the metastable $(\text{Cr}_{1-x}\text{Ti}_x)\text{C}_y$ phase (see discussion above). Using thermodynamic considerations and Ti-C phase diagram it could be argued that a Ti-C film with a substoichiometric composition of the carbide ($y<1$) cannot contain an additional a-C phase. However, the sputtering process is carried out far from equilibrium and the metastable condition is more of a rule than exception. The phase diagrams, on the other hand, are valid for bulk alloys in thermodynamic equilibrium and can generally be not applied unconditionally to thin film alloys. Several authors have demonstrated that stoichiometric Ti-C is formed together with an amorphous C phase (see, e.g., ref. [31,32]). Also, it can be argued that the presence of vacancies in the crystalline carbide would affect the lattice constant and explain the reduction in cell size.

As can be seen in ref. [32], however, the influence of C vacancies on lattice parameter is small compared to the observed variations in Fig. 3.

4.2 Mechanical properties

The variation of hardness in dependence of x shows that for both LC and HC series the amorphous films are less hard than most of the crystalline films. This, together with the particular case of the steep increase in hardness of the material induced by the start of crystallization (at $x=0.28$ for series LC, and $x=0.16$ for series HC) proves that mechanical characteristics of the material, modulus, and hardness, depend more on the film structure than its composition. Similar type of significant hardening upon crystallization has been observed before by Ziebert et al. for sputtered Cr-C films [14]. Differently from the binary Cr-C phases where hardness can be clearly correlated to the level of crystallization for the Cr-Ti-C films an increasing trend in hardness with the increasing level of crystallization is only detected for ternary LC films. Starting with the metal-rich LC series in Fig. 7, the amorphous films have hardness value between 16 and 17 GPa which after crystallization increases with higher Cr contents to over 28 GPa for $x=0.71$ compared to slightly over 26 GPa for a pure Ti-C film. Such maximum in hardness for ternary phase can be connected to a solution hardening of the carbide. This phenomenon should not be excluded in the HC series, although the high Cr content films for $x=0.7$ displays minimum in hardness value. The metal atoms, as already shown by XPS results, are in this case bound into the crystalline phase leaving the soft mostly a-C containing phase as amorphous matrix between the crystalline grains what results in an effective diminishing of the material hardness. To examine the elasticity of the material in dependence of x the H/E value is compared for all investigated samples. Since the elastic modulus exhibits the same change trend as hardness for both film series (see fig. 7) it is not surprising that the H/E value increases for LC films continuously from 46.7×10^{-3} at $x=0$ to 78.3×10^{-3} at $x=1$. The lower the H/E value, the more plastically and more brittle the material behaves [33]. For the ideally plastic behavior, $H/E=0$ while ideally elastic behavior would be indicated by $H/E=0.17$ [34]. The reduced H/E values with the decreasing x for the LC films can be correlated to the microindents of the corresponding films with increased pile-up for the low x

values, which indicates more plastic deformation prone material. The benefits of reducing E for material's mechanical properties in terms of increased wear resistance and increased fracture-toughness have been already demonstrated by Leyland *et al.* [33]. The clear trend of the crack propagation for different Cr-Ti-C films is, however, not visible with the exception for the pure Cr-C and Ti-C films, where no visible cracks are present. This confirms [35] that crack propagation is a complex phenomenon that depends on several factors, and cannot be related exclusively to plasticity of the material. Moreover, although the H/E ratio should give an indication of the tendency of the material to behave more plastically or elastically, the different materials may behave differently for similar H/E ratios [36]. This is in our case further shown by HC films for which no microindent related pile-up of the material can be seen, but pronounced cracks can be seen for all examined HC films. Since HC films are softer compared to most of the LC films it can be concluded that the mechanical behavior, including crack propagation, of the films must be dependent on both parameters, composition and crystalline structure. The deviation of the H/E ratio for the HC pure Ti-C films suggests that nearly all Ti is bound to C atoms forming a carbide, leaving an almost pure a-C matrix that increases significantly the susceptibility of the material towards plastic deformation.

5. Conclusions

This study shows that Ti has a strong effect on the crystallization of Cr-C films. Sputtered Cr-C films are typically amorphous in contrast to Ti-C films, which form films with crystalline Ti-C in a cubic B1 structure. The Cr-C films further have two amorphous phases of a-Cr₇C₃ and a-C. The final phase distribution was detected as a complex mixture of a cubic (Cr_{1-x}Ti_x)C_y phase, a-C, and possibly some amorphous Cr-C.

The addition of 15 at% of Ti to the Cr-C films leads to the formation of a crystalline carbide with cubic B1-type structure, with Ti and Cr on the metal sites. The cell parameter for this metastable solid solution depends on the Ti content and follows for the Vegards law for C-rich films. For the more metal-rich films, the deviation from Vegard's law indicates that some Cr remains present in an amorphous phase. The

increasing content of Ti in the films causes increase of hardness of the films and a general increase of H/E ratio. The latter indicates that tougher and less brittle films are formed for higher Ti content. For ternary phase films, an observed maximum in hardness indicates a solution hardening of the carbide.

Acknowledgements

The authors wish to thank the Swedish Research Council (VR) and the Swedish Foundation for Strategic Research (SSF) MS2E for the financial support.

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Figure captions

Fig. 1. Ternary plot for the composition of films investigated in this work.

Fig. 2. GI-XRD of the investigated $(\text{Cr}_{1-x}\text{Ti}_x)\text{C}_y$ films for different x for (a) LC and (b) HC sample series.

Fig. 3. Lattice parameter of the $(\text{Cr}_{1-x}\text{Ti}_x)\text{C}_y$ films for different x for both sample series. The full line connects literature lattice parameters for pure CrC; $x=0$ (4.1 Å) and TiC; $x=1$ (4.32 Å) depicting Vegard's law. The dotted line is a linear fit to LC series values.

Fig. 4. TEM micrographs with SAED insets for four representative samples from the LC series; (a) $(\text{Cr}_{1-x}\text{Ti}_x)\text{C}_y$ containing 6.9 at% Ti ($x=0.1$) with columnar structure shown on lower resolution image on inset (I), (b) CrTiC containing 18.9 at% Ti ($x=0.28$), (c) CrTiC containing 45.6 at% Ti ($x=0.71$), and (d) pure Ti-C ($x=1$).

Fig. 5. SEM images of the four representative samples from the LC series; (a) pure CrC ($x=0$), (b) CrTiC containing 18.9 at.% Ti ($x=0.28$), (c) CrTiC containing 45.6 at.% Ti ($x=0.71$), and (d) pure TiC ($x=1$).

Fig. 6. C1s XPS peak for $(\text{Cr}_{1-x}\text{Ti}_x)\text{C}_y$ films in relation to various Ti content for a) LC series films and b) HC series films. (a) inset, variation of proportion of C-C in C1s peak for different x for both samples series (lines are only to guide the eye). (b) inset, binding energy variation of C-Me part of C1s peak for different x for both samples series.

Fig. 7. (a) Hardness and (b) modulus of the CrTiC films as a function of the Ti content in the films obtained by nanoindentation testing using Berkovich indenter. (a) inset, load-unload curves for two representative LC series samples containing 10.6 at.% ($x=0.15$) and 45.6 at.% ($x=0.71$) of Ti.

Fig. 8. Hardness to modulus dependence on x for LC and HC series films.

Fig. 9. SEM images of microindents (100 g load) on six representative films of LC series; (a) $x=0$, (b) $x=0.1$, (c) $x=0.15$, (d) $x=0.44$, (e) $x=0.71$, and (f) $x=1$.

Fig. 10. SEM images of microindents (100 g load) on four representative films of HC series; (a) $x=0$, (b) $x=0.16$, (c) $x=0.7$, and (d) $x=1$.