The structure and mechanical properties of Cr-based Cr-Ti alloy films

Gang Liu1,∗, Miao Wang2, Jianjun Xu3, Min Huang3, Chen Wang4, Yabo Fu1, Changhong Lin1, Jianbo Wu1 and Vladimir A Levchenko1,∗∗
1 Institute of Advanced Coating Materials, Zhejiang Provincial Key Laboratory for Cutting Tools, Taizhou University, Jiaojiang 318000, Zhejiang, People’s Republic of China
2 Technical Research and Development Department, Western BaoDe Technologies Co., Ltd, Xi’an 710201, People’s Republic of China
3 Analytical & Testing Center, Northwestern Polytechnical University, Xi’an 710201, People’s Republic of China
4 School of Materials Science and Engineering, Xi’an Shiyou University, Xi’an 710201, People’s Republic of China
5 Faculty of Chemistry, Lomonosov Moscow State University, GSP-1, Leninskie Gory, Moscow, 119991, Russia
∗ Authors to whom any correspondence should be addressed.

E-mail: liugang2186@163.com and vladlev@yahoo.com

Keywords: Cr-ti alloy film, microstructure, hardness, modulus, magnetron sputtering

Abstract

Previous studies have dealt with Cr and its alloy films that exhibit promising characteristics as surface modification layers for antiwear, anticorrosive, and decorative applications. However, the effect of Ti alloying on the structure and mechanical properties of Cr films has not been studied. This work aimed to the structure and mechanical properties of Cr-Ti alloy films in the Cr-rich side. To this end, pure Cr, Cr-6 at.% Ti, Cr-11 at.% Ti, Cr-16 at.% Ti, and Cr-21 at.% Ti alloy films were prepared by magnetron sputtering, and the structure and mechanical properties of the films were evaluated. The results indicated that all the films exhibited a Cr-based growth with body-centered cubic structure, and increasing the Ti content decreased the (110) orientation growth of Cr basis. Ti alloying increased the hardness of the films, while leading to a monotonic decrease in the modulus of the films. The first-principles method was employed to demonstrate that the reduced modulus was determined by the Ti alloying degree, rather than the orientation evolution of the films. The analysis of H/E value suggested that the wear resistance of the films was improved by Ti alloying. The mechanical properties of present Cr-Ti alloy films, and other Cr-based alloy films or metallic glasses in publications were compared and discussed. We proposed that Ti alloying is a considerable way to explore advanced mechanical properties of Cr-based alloy films.

1. Introduction

Cr films attract a lot of interest due to their high mechanical strength, excellent resistance to corrosion and oxidation, and metallic lustre. These advantages generate large usage of Cr films as antiwear and anticorrosive surfaces with decorative functionalities [1, 2]. Physical vapour deposition (PVD) processes, such as magnetron sputtering [3, 4], thermal evaporation [5], electrodepositing [1], and cold spraying [6], are mostly used to produce Cr films in different coating systems. The relationships among process parameter, film structure, and properties have been extensively studied because controlling the process parameters is a basic way to optimize the structure and properties of the films [7–9]. Moreover, the alloy composition is another important factor on the structure and properties of film materials. Therefore, the present work is aimed to investigate the structure and properties of Cr alloy films.

Generally, the addition of alloy elements can improve mechanical properties of metallic materials if the effects of alloy elements are utilised adequately. On one hand, solid solution hardening is an efficient method to improve the strength of metallic materials. On the other hand, alloying could change the growth morphology, crystalline size, crystallinity, crystalline orientation, and stress state of the films [10–15], all of which can produce substantial effects on their properties. These facts have adequately promoted extensive studies on binary alloy films, such as Zr-Ti [16], Ti-Nb [17, 18], Ni-W [16], Mg-Ti [19], Cu-Mo [20], and Ag-Cr [21] systems. Regarding
to Cr alloy systems, Chen et al. [22] demonstrated that Cr-Al alloy coatings could have much better oxidation resistance than pure Cr coatings. Li et al. [23] demonstrated that Cr-Ni alloy films could exhibit excellent high-temperature wear resistance. Wang et al. [24] demonstrated that Cr-Fe interlayers could improve the wetting behaviours between Al and Zr2O3/Al2O3 composites. The abovementioned results indicate that alloying of Cr films is a noteworthy attempt to explore the enhanced mechanical and functional properties of the films.

Ti has excellent anticorrosive and decoration properties, which is similar to Cr element. Previous studies have focused their attention on corrosion and oxidation resistances of binary Cr-Ti alloy films as an important issue of these materials [25–29]. More recently, Zhang et al. [30] investigated the structure and mechanical properties of Cr-Ti alloy films, however, in the Ti-rich region, and they found that mechanical properties of the films were highly related to the phase constitution of Ti basis. Compared to Ti-based growth, Cr-based growth is a preferred configuration to provide high hardness and strength [31], and good wear resistance [32, 33]. Furthermore, Cr-based growth is expected to decrease the fabricating cost because of the low cost of Cr element. As a result, Lee et al. [34] proposed the practical application of Cr-based Cr100−xTi x (x = 0–19 at.%) film as an underlayer for magnetic coating systems. However, to the best of our knowledge, the structure and mechanical properties of Cr-Ti alloy films in the Cr-rich region have not been studied.

This work focused on the structure and mechanical properties of Cr-Ti alloy films in the Cr-rich region. The pure Cr and Cr-Ti alloy films were prepared by magnetron sputtering processes. Firstly, the structure evolutions of the films with increasing Ti content were studied. Secondly, the mechanical property modifications introduced by structure evolution were investigated. Finally, the mechanical properties of the present Cr-Ti alloy films and other Cr alloy systems in publications were compared and discussed.

2. Experimental

2.1. Film preparation

Cr-Ti alloy films were prepared using high power impulse magnetron sputtering (HiPIMS) processes by co-depositing pure Cr and Ti targets (Cr 99.8%, Ti 99.95%, 500 mm × 94 mm × 8 mm) which were connected to a TruPlasma 4000 G2 HiPIMS source (Freiburg, GER), respective. The pulse width was 200 μs, and the pulse frequency was 1500 Hz, yielding a duty cycle of 21% for all depositions. The applied voltage to the Cr target was ≈ 470 V with an average power of 4.6 kW for pure Cr deposition, and 4.3, 4.2, 4.1, and 4.0 kW for co-deposition. The applied voltage to the Ti target was ≈ 350 V with an average power of 0.7, 1.3, 1.9, and 2.5 kW. Five groups of samples, including pure Cr films and four Cr-Ti alloy films with increasing Ti content, were prepared. The HiPIMS conditions were also employed in combination with a negative polarisation to the substrate (bias of −100 V) using a TruPlasma DC-pulsed source working at a frequency of 100 kHz and 90% duty cycle.

P-type (100) silicon wafers were used as substrates. Silicon wafers were adopted for the observation on the fractographies of the films. Conductive ability of the wafers was utilized to enhance substrate current density under bias conditions, which may improve the particle bombardment effect on the growing surfaces of the films during depositions. The wafers were chemically cleaned in an ultrasonic bath with acetone and isopropyl alcohol (for 20 min each), followed by Ar etching for 30 min at 800 V inside the chamber before deposition. In addition, the wafers were fixed at the profile of a 250 mm diameter cylindrical steel frame which was rotating at 25 Hz during deposition. The separation between the profile of frame and the target was 150 mm. A base pressure of 7.0 × 10−6 Pa was achieved, and the gas flow of Ar was fixed at 80 sccm for a working pressure ≈ 0.5 Pa. The deposition temperature was fixed at 200 °C and the deposition time was fixed at 180 min. After each deposition, the temperature was maintained for 20 min, and then the films were cooled to 30 °C in the vacuum.

2.2. Film characterization

We used a PANalitical X’Pert PRo MPD instrument (Almelo, Netherlands) for the preliminary analysis of the phases in the samples. The XRD patterns were obtained using CuKα (40 kV, 30 mA) radiation with grazing incidence of 2°, and step size of 0.02°. The diffraction angle ranged from 30° to 90°. A Tescan MIRA3 XMU SEM apparatus (Brno, Czech Republic) was used to obtain the growth morphologies of the films. Bulk compositions of the films were detected using a SEM-based INCA energy dispersive spectrometer (EDS) with an X-MAX detector (Oxford Instruments, UK). The calibration was performed using a Ti standard, and the quantisation was processed with a built-in XPP correction procedure. The film thickness was measured using SEM observations. A summary of the main deposition parameters, film thickness, and composition obtained using EDS are displayed in table 1.

TEM and STEM analyses were performed using a FEI Themis Z spherical aberration correction TEM (Hillsboro, OR). Prior to the analyses, the cross section of the sample was prepared using a focused ion beam (FIB) system equipped with a Tescan LYRA3 GMH scanning electron microscope (SEM; Brno, Czech Republic).
Table 1. Summary of the deposition parameters, including deposition time and average power of Cr and Ti targets, film thickness, and elemental composition determined by EDS.

| Sample # | Deposition time (min) | Average power (KW) | Working pressure (Pa) | Thickness (μm) | Cr (at.%) | Ti (at.%) |
|----------|-----------------------|---------------------|-----------------------|---------------|-----------|-----------|
| 1        | 120                   | 4.6                 | 0.5                   | 1.90          | 100       | —         |
| 2        | 120                   | 4.3                 | 0.7                   | 1.83          | 94        | 6         |
| 3        | 120                   | 4.2                 | 1.3                   | 2.12          | 89        | 11        |
| 4        | 120                   | 4.1                 | 1.9                   | 2.47          | 84        | 16        |
| 5        | 120                   | 4.0                 | 2.5                   | 2.38          | 79        | 21        |

Bright field (BF) technique was used to show the growth morphology of the film. The bulk composition was measured by STEM-EDS technique which was performed on an initial High-angle annular dark field (HAADF) image. Selected area electron diffraction (SAED), and high resolution transmission electron microscopy (HRTEM) with fast Fourier transform (FFT) images were used to reveal the crystalline orientation evolution which was affected by the addition of Ti alloy elements.

Nanoindentation tests were performed using an Agilent U9820A Nano Indenter G200 (Santa Clara, CA) with a diamond Berkovich indenter. The Agilent Continuous Stiffness Measurement (CSM) option was used to measure the mechanical properties as a continuous function of penetration depth with a surface approach velocity of 10 nm s⁻¹, and a strain rate target of 0.05 s⁻¹. The value of the Poisson ratio was 0.25. To minimise the substrate influence, less than one-tenth of the film thickness was taken into consideration. We averaged a total of nine indents to determine the mean hardness (H) and modulus (E) for the sample at each condition.

2.3. Calculation method

A virtual-crystal approximation (VCA) method within the density functional theory (DFT) framework [35] was used to investigate the effect of Ti alloying and crystalline orientation on the modulus of the films from a theoretical perspective. The VCA method is superior in terms of simplicity and efficiency, and has been used in the theoretical research of various alloy systems, including binary [36–38] and ternary [39] alloys, high-entropy alloys [40, 41], alloy carbides [42, 43], and nitrides [44]. In a VCA model of Cr-Ti solid solution, if two elements Cr and Ti are randomly distributed in the atomic ratio of x:1-x, a virtual element CrₓTi₁₋ₓ will be produced to replace each alloying element Cr and Ti at the lattice site. In this work, the value of X was set as a continuous variable from 1 to 0.78 with a step size of 0.01 according to the EDS results displayed in Tab. 1. The following calculations were performed using the CASTEP module within the Materials Studio software package 7.0. Firstly, the pure Cr unit cell (X = 1) was optimised in appropriate convergence conditions to obtain a lattice constant of 2.8731 Å. This result is very close to the value 2.8935 Å obtained by the position of (110) main peak of present pure Cr reflections, and the standard value 2.8839 Å of pure Cr (PDF card no. 06-0694). Secondly, the VCA models (0.99 ≥ X ≥ 0.78) were optimised in similar conditions, and the elastic modulus on each crystalline orientation including (100), (110), (111), (211), and (310), obtained by continuously changing the X value, were given by [45–47]:

\[
\frac{1}{E_{hkl}} = S_{11} - 2\left(S_{11} - S_{12} - \frac{S_{44}}{2}\right)(l_1^2 l_2^2 + l_2^2 l_3^2 + l_3^2 l_1^2)
\]

where S₁₁, S₁₂, and S₄₄ are elastic compliances. The terms l₁, l₂, and l₃ are the direction cosines: the cosine of the angle between the direction of interest [hkl] and the X-, Y-, and Z-axes (the (100) directions).

3. Results and discussion

Figure 1 displays the XRD patterns of pure Cr and Cr-Ti alloy films with increasing Ti alloying content. The pure Cr, Cr-6 at.% Ti, and Cr-11 at.% Ti films exhibit three reflections: Cr(110), Cr(200), and Cr(211), and the Cr-16 at.% Ti and Cr-21 at.% Ti alloy films exhibit two reflections: Cr(110) and Cr(211). Therefore, the present Cr-Ti alloy films are Cr-based solid solutions with body-centred cubic (BCC) structure. The Cr(110) peaks are left shifted and the peak width becomes broader as the Ti content rises. The reason behind the left shift might be mostly the incorporation of larger Ti atoms (1.45 Å) into the Cr lattice with a smaller atomic radius (1.27 Å), which leads to an increase in the average of the nearest neighbour distance (i.e., interplanar spacing). The peak broaden indicates that the crystalline size of the Cr-Ti alloy films was refined by the alloying processes. This is
because the incorporation of Ti element will increase the defect density, and disturb the crystalline growth of the Cr basis during the growth of the films.

According to the Cr-Ti binary equilibrium phase diagram [48], the solid solubility of Ti in BCC Cr basis is below 2 at.% at 600 °C. A heating treatment at about 1250 °C is needed to produce BCC-type Cr-20 at.% Ti solid solution under equilibrium conditions. However, we produced BCC-type Cr-based Cr-Ti alloy films with Ti content up to 21 at..% That is to say, the present Cr-Ti alloy films are supersaturated solid solutions, and they are not stable in thermodynamics. The supersaturated solution behaviours in the films can be attributed to the particle bombardment process of magnetron sputtering. It means an atomic scale heating on the growing surface of the films which companies with a highly non-equilibrium cooling process [49, 50]. During the process, the solid solution with enhanced solubility at high temperature can be formed by the energy from particle bombardment, and then fast froze into a metastable state, i.e., supersaturated state. Similar results have been widely demonstrated in sputtered-deposited binary alloy systems, such as Mo-Cu [51], Al-Mo [52], and Ni-Zr [53] alloy films.

Figure 2 displays the SEM fractographies of present Cr and Cr-Ti alloy films with increasing Ti content. From figures 2(a)–(c), pure Cr, Cr-6 at.% Ti, and Cr-11 at.% Ti films all exhibit a columnar morphology. From figures 2(d)–(e), Cr-16 at.% Ti and Cr-21 at.% Ti alloy films also exhibit a columnar growth, while the size of the column becomes more finer, and the boundary of the column becomes blurred, which suggests the decomposition of the columnar growth with the increasing Ti content. Previous studies [9] demonstrated that the decomposition of columnar growth is highly related to the change of crystalline orientation of the films. Therefore, TEM analyses of the Cr-6 at.% and Cr-21 at.% Ti alloy films were both performed to reveal the crystalline orientation evolution of the films. Firstly, the elemental composition of the Cr-6 at.% and Cr-21 at.% Ti alloy films were verified by STEM-EDS technique, as shown in figure 3. The results are fully consistent with those obtained by SEM-EDS (Tab. 1). Subsequently, we focused on the boundary zone between two columnar crystals in the BF mode, as indexed by the white frames in figure 3(a), (b). Then HRTEM images were obtained unanimously in the incident direction [111] of the left crystal of the boundary line, which are shown in figures 4(c), (d). For the Cr-6 at.% Ti alloy film, figure 4(c) shows that the (110) lattice fringes of two neighbouring crystals are nearly parallel. Moreover, the FFT image on the left of the boundary line provides a complete pattern, while the FFT image on the right only displays the (110) spot. This result indicates that the neighbouring crystals grow consistently in the (110) orientation in the Cr-6 at.% Ti alloy film. For the Cr-21 at.% Ti alloy film, figure 4(d) shows that clear (110) lattice fringes are observed on the left of the boundary line, while no lattice fringe can be observed on the right. Accordingly, the FFT on the left exhibits a complete pattern, while no spot can be obtained by the FFT on the right, indicating that the two neighbouring crystals have completely different growth orientations. By comparing the HRTEM results of the two films, it can be demonstrated that increasing the Ti content will enhance the degree of misorientation between the neighbouring crystals in the Cr-Ti alloy films. Finally, SAED patterns were obtained both at the upper and lower portions of the cross section of the films, which were indexed by the two circles in the BF images. The results in figures 4(e), (f) and figures 4(g), (h) both show that the upper and lower portions of the film yield a similar pattern of Cr lattice, suggesting that
the film has a uniform growth during the deposition process. The SAED pattern of the Cr-6 at.% Ti alloy film shows an intensive reflection only in the (110) orientation, while the reflection in other orientations seems weak or dispersive, as shown in figures 4(e), (f). When the Ti content increases to 21 at.%, the SAED pattern change into a circular-distributed form, which suggests a reduced orientation growth at high Ti content condition, as shown in figures 4(g), (h). To note that, no additional phase could be identified except the Cr-based phase in above TEM analyses. This result confirms that the present Cr-Ti alloy films are BCC-type Cr-based solid solutions as indicated by the XRD results. Another important conclusion that can be drawn by the TEM analyses is that Ti alloying process decreases the (110) orientation growth of Cr basis.

The structure zone model (SZM) from Barna et al [14, 54] gives detail on the orientation development in metallic films. The orientation development in the films stems from the minimization of overall surface and interface energies. During the process, crystalizes with densest planes are typically selected, so the film will develop an oriented structure: that is, (110) for BCC, (111) for FCC, and (0001) for HCP. This has been extensively demonstrated in publications [8, 9, 20]. In addition, the SZM also illustrates that the incorporation of
additives or impurities could decline the orientation growth of the basic structure of the films. For example, the incorporation of Zr will decrease the (110) growth of BCC Ti-Nb basis [12], and the incorporation of O will decrease the (111) growth of FCC Al basis [54]. It can be explained that the presence of alloying or impurity elements and their segregation to surfaces and grain boundaries have an inhibition effect on the orientation development of the basic structures. In present work, we report that the BCC Cr film could have a (110) orientation growth, and Ti alloying process could decrease the orientation growth of Cr basis. These results agree well with the SZM, and the experimental results in publications.

Figure 5(a) shows the hardness of present pure Cr and Cr-Ti alloy films as a function of penetration depth. The hardness of the films reaches a constant value when the penetration depth reaches 170 nm. The summary of hardness values of the films as a function of Ti content is shown in figure 5(d). The data indicate that: (i) the Cr-6 at.% Ti alloy films have a significantly improved hardness (≈ 12.5 GPa) compared to that of pure Cr films (≈ 9 GPa [55, 56]). Such case is attributed to the solid solution strengthening effect and the fine-grain strengthening effect which are both caused by the Ti alloying process. (ii) Cr-Ti alloy films exhibit a slight decrease in the hardness when the Ti content exceeds 6 at%. This result can be related to the high degree of misorientation between the neighbouring grains in the Cr-Ti alloy films containing high Ti contents, which has been demonstrated by the HRTEM analyses in figure 4(d). As we know, the volume fraction of grain boundaries increases obviously in nanometers. Therefore, the deformation resistance of grain boundaries becomes a crucial factor influencing the film hardness. In the highly textured film, the sliding or movement of grain boundaries is difficult because of the increased degree of coherency associated grain boundaries, i.e., the misorientations between the neighbouring grains are small [57]. When the misorientation between the neighbouring grains increases, the sliding or movement of grain boundary become easier, which could decrease the deformation resistance of grain boundaries, and thus decrease the film hardness. The so-called texture strengthening effect has been demonstrated in nanometals, such as Zr-Ti [13] alloy films or Ni nanophases [58]. Therefore, we can infer that the weakened orientation growth denotes the relatively low hardness of Cr-Ti alloy films containing Ti content exceeds 6 at.%.
Figure 5 shows the modulus of pure Cr and Cr-Ti alloy films as a function of penetration depth. The modulus of the films reaches a constant value when the penetration depth reaches 150 nm. The modulus values of the films as a function of Ti content are summarized in Figure 5 (d). The data show that the modulus decreases monotonically from 270.7 to 188.5 GPa with the increase in Ti content. The XRD and TEM results demonstrate that all the Cr-Ti alloy films grow in BCC-type Cr-based solid solution structure. As a result, two critical factors, including chemical composition and crystalline orientation of the films, can be considered for the change in the modulus. The theoretical results on the modulus of the films with different Ti contents and crystalline orientations obtained using VCA are presented in Figure 5 (c). The data indicates that: (i) the increasing of Ti content unanimously decreases the modulus of Cr lattice for all conditions, although the curves are not monotonous in some intervals; (ii) the (110) orientation is one of crystalline orientations which have relatively low modulus, and thus the change from (110) to other orientations or polycrystalline growth would increase the modulus. To note that the (111) orientation has the lowest modulus, however, the (111) growth is the weakest in Cr lattice according to PDF card no. 06-0694. In conclusion, theoretical results demonstrate that increasing Ti content and declining (110) orientation growth will have negative and positive effects on the modulus of the films, respectively. In terms of the nanoindentation results, the pure Cr film with (110) growth has a modulus of 270.7 GPa, which is close to the theoretical result of 290.2 GPa on (110) orientation. This discrepancy can be attributed to the high-density defects in the real samples because of the highly non-equilibrium deposition processes. When the Ti content rises, the films show a decrease of modulus, which agrees well with the theoretical results. Therefore, we can derive that the increasing Ti content, rather than the declining (110) texture growth, determines the change of the modulus of the films.

The ultimate tensile strength $\sigma_{UTS}$ of ductile metallic and alloy films can be estimated from the formula $H \approx 3\sigma_{UTS}$, here H is the hardness of the film [59]. In addition, the evaluation of wear resistance of the film can be proxied by the value of $H/E$ [60–62]. Generally, materials possessing a higher $H/E$ ratio often exhibit higher wear resistance. So we can investigate the effects of Ti alloying on the ultimate tensile strength and wear resistance of the films based on the nanoindentation results. Figure 6 depicts the values of $\sigma_{UTS}$ and $H/E$ obtained for present pure Cr and Cr-Ti alloy films (red region). It is shown that: (i) the values of $\sigma_{UTS}$ obtained for Cr-Ti alloy films ($\approx 4$ GPa) are higher than that obtained for pure Cr film ($\approx 3$ GPa); (ii) the value of $H/E$ increases from 0.037 to 0.063 as the Ti content rises. These results indicate that Ti alloying could improve
ultimate tensile strength and wear resistance of the films. We note that the increase of H/E value is denoted by the enhanced hardness when the Ti content below 6 at.%, while by the reduced modulus when the Ti content exceeds 6 at.%, as illustrated in figure 5(d). The enhanced hardness means larger resistance to plastic deformation for compressed film surface during the sliding processes, while the reduced modulus means the stresses under the contact loading can be distributed over a wider area. Accordingly, the changes of H and E values suggest that the above two effects are both conducive to the enhanced wear resistance of the films by Ti alloying. This result is different from some publications on binary alloy films [15, 30], in which the alloying processes could improve the values of H/E primarily by a substantial hardening effect, despite often triggering a slight change in the modulus. For example, Wang et al [15] reported that the hardness of Zr-Ti alloy films was much more sensitive to Zr/Ti ratio than modulus was. Zhang et al [30] found that Cr alloying of Ti films could largely increase the film hardness, but slightly increase the film modulus despite of the phase evolution induced by Cr additives. These studies show a feasible way to improve the wear resistance of the films based on the control of H/E, with respect to different effects of alloying process on film hardness and modulus.

Figure 6 also depicts the values of σ_{UTS} and H/E obtained for Ti-based Ti-Cr alloy films [36, 63], Cr-based Cr-Cu alloy films [36], Cr-based Cr-Ni alloy films [64], and Cr-based bulk metallic glasses (BMGs) [31, 65, 66] for a comparison. In the group of Cr alloy films (grey region), the present Cr-Ti alloy films exhibit a higher value region of σ_{UTS} than the Cr-Cu and Cr-Ni alloy films, suggesting that Ti alloying is a preferred strengthening way among the alloying processes considered. This result can be simply explained by the solution strengthening effect which is highly related to the disparity of atomic radius between the basic and additive elements. The atomic radius of Ti (1.45 Å) is much larger than that of Cr (1.27 Å), while the atomic radiiuses of Cu and Ni (1.28 and 1.24 Å) are very close to that of Cr. Therefore, Ti alloying process can cause great lattice distortions in Cr basis, and thus produce much stronger solution strengthening effect than Cu and Ni alloying processes. For the concerned Cr-Ti binary systems, the Cr-based Cr-Ti alloy films (red region) are characterized by relatively high values of σ_{UTS} compared to the Ti-based Ti-Cr alloy films considered (green region), while inversely the Ti-based Ti-Cr alloy films may have a higher value of H/E than the Cr-based ones. The advantage of H/E of the Ti-based alloy films can be explained by the intrinsic low modulus of Ti element. The Cr-based BMGs (yellow region) undoubtly exhibit the highest value of σ_{UTS} among the materials considered. It is because BMGs have the extremely strong strengthening effect from the metastable multielement structures. In spite of this, the Cr-based Cr-Ti alloy films could possess the values of H/E comparable to those of BMGs, which are attributed to the significantly reduced modulus under Ti alloying conditions. It follows from the above that Ti alloying is considerable way to explore the enhanced mechanical properties of Cr-based alloy films.

4. Conclusions

This work focused on the structure and mechanical properties of Cr-based Cr-Ti alloy films. Pure Cr, Cr-6 at.% Ti, Cr-11 at.% Ti, Cr-16 at.% Ti, and Cr-21 at.% Ti alloy films were prepared using magnetron sputtering.
process by co-depositing pure Cr and Ti targets, respectively. We investigated the structural properties of the films by XRD, SEM, and TEM techniques. The results show that all the films have a body-centered cubic Cr-based solid solution structure, and Ti alloying decreases the (110) orientation of Cr basis. We used nanoindentation technique to assess hardness and modulus of the films. The results show that Ti alloying not only increases the hardness, but also decreases the modulus of the films. We investigated the modulus of the films using first-principles calculations by considering the effects of chemical composition and crystalline orientations. The calculation results demonstrate that Ti content plays a key role in determining the decrease in the modulus of the films. We evaluated the effect of Ti alloying on wear resistance of the films by the H/E values. The result shows that the H/E value increases from 0.037 to 0.063, suggesting an improvement of wear resistance of the films by Ti alloying process. Finally, we compared the mechanical properties of present Cr-Ti alloy films with those of other Cr alloy films or Cr-based BMGs in publications. The results suggest that Ti alloying process is a developable way to explore the enhanced mechanical properties of Cr-based alloy films.

Acknowledgments

This work was fully sponsored by National key Research and Development plan of China [Grant No. 2018YFB1107305], National natural Science Foundation of China [Grant No. 51902254], Project of National Joint Engineering Research Center for abrasion control and molding of metal materials of China [Grant No. HKDNM2019024], Zhejiang Provincial Natural Science Foundation of China [Grant No. LGG20E010004], [Grant No. LZZ20E020001], and Taizhou Science and Technology Project [Grant No. 1902gy16]. The computational work was supported by the National Supercomputing Centre in Shenzhen, P R China.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Credit authorship contribution statement

Gang Liu: Conceptualization, Methodology, Writing-original draft, Writing-review & editing, Data curation, Supervision. Miao Wang: Methodology, Writing-review & editing. Jianjun Xu: Methodology, Data curation. Min Huang: Methodology, Data curation. Chen Wang: Data curation. Yabo Fu: Data curation. Changhong Lin: Data curation. Jianbo Wu: Supervision, Data curation. Vladimir A. Levchenko: Project, Supervision.

ORCID iDs

Gang Liu @ https://orcid.org/0000-0001-7165-8959

References

[1] Leimbach M, Tscharc Z, Zapf D, Kurniawan M, Schmidt U and Bund A 2019 Relation between color and surface morphology of electrodeposited chromium for decorative applications J. Electrochem. Soc. 166 D205–11
[2] Leimbach M, Tscharc Z, Schmidt U and Bund A 2018 Electrochemical characterization of chromium deposition from trivalent solutions for decorative applications by EQCM and near-surface pH measurements Electrochim. Acta 270 104–9
[3] Sidelev D V, Bleykher G A, Bestetti M, Krivobokov V P, Vicenzo A, Franz S and Brunella M F 2017 A comparative study on the properties of chromium coatings deposited by magnetron sputtering with hot and cooled target Vacuum 143 479–85
[4] Salo S A, Abdallah B, Akel M and Kakhia M 2020 Structural and plasma characterization of the power effect on the chromium thin film deposited by DC magnetron sputtering Optoelectronics Letters 16 369–72
[5] Udachan S L, Ayachit N H, Udachan I A, Siddanna S, Kolkundi S S and Ramya S 2021 Infrared optical constants of chromium nanofilms Journal of Physics Conf. Series 1762 012026
[6] Maier B, Yeom H, Johnson G, Dabney T, Walters J, Xu P, Romero J, Shah H and Sridharan K 2019 Development of cold spray chromium coatings for improved accident tolerant zirconium-alloy cladding J. Nucl. Mater. 519 247–54
[7] Du Y, Meng X and Gao X 2019 Variations of the microstructure and the optical and electrical properties with sputtering power for direct-current magnetron sputtered indium-doped CuO thin films at room temperature Thin Solid Films 684 53–8
[8] Liu G, Yang Y, Jin N, Luo X, Huang B, Li P and Kou Z 2018 The structural characterizations of Ti-17 alloy films prepared by magnetron sputtering Applied Surface Science 427, Part B 427 774–81
[9] Liu G, Yang Y, Huang B, Luo X, Ouyang S, Zhao G, Jin N and Li P 2016 Effects of substrate temperature on the structure, residual stress and nanohardness of Ti6Al4V films prepared by magnetron sputtering Appl. Surf. Sci. 370 53–8
[10] Esmaeili A, Mir N and Mohammadi R 2021 Influence of W content on microstructure and surface morphology of hard Ni-W films fabricated by magnetron co-sputtering Journal of Vacuum Science & Technology A 39 033405
[11] Liu G, Yang Y, Luo X, Huang B and Li P 2017 The phase, morphology and surface characterization of Ti-Mo alloy films prepared by magnetron sputtering RSC Adv. 7 52595–603
[12] Gonzalez E D, Fukumasu N K, Afonso C R M and Nascente P A P 2021 Impact of Zr content on the nanostructure, mechanical, and tribological behaviors of Ti-Nb-Zr ternary alloy coatings Thin Solid Films 721 138565
[13] Frutos E, Karlík M, Jiménez J A, Langhanšová H, Liesková J and Polcar T 2018 Development of new 3/a°-Ti-Nb-Zr biocompatible coating with low Young’s modulus and high toughness for medical applications Mater. Des. 142 44–55
[14] Petrov I, Barna P B, Hultman L and Greene J E 2003 Microstructural evolution during film growth Journal of Vacuum Science & Technology A 21 S117–28
[15] Wang W, Zhan P, Xie Z, Li Z and Zhang Z 2014 Mechanical property improvement by texture control of magnetron co-sputtered Zr-Ti films J. Appl. Phys. 115 043524
[16] Zeman P, Zítek M, Zoujáková S and Čerství R 2017 Amorphous Zr-Cu thin-film alloys with metallic glass behavior J. Alloys Compd. 696 1298–306
[17] Gonzalez E D, Niemeyer T C, Afonso C R M and Nascente P A 2016 Ti-Nb thin films deposited by magnetron sputtering on stainless steel Journal of Vacuum Science & Technology A 34 021511
[18] Gonzalez E D, Afonso C R M and Nascente P A 2018 Nanostructural characterization of sputter deposited Ti-Nb coatings byautomated crystallographic orientation mapping Thin Solid Films 661 92–7
[19] Song G L, Unocic K A, Meyer H, Cakmak E, Brady M P, Gannon P E, Himmer P and Andrews Q 2016 The corrosion and passivity of sputtered Mg-Ti alloys Corros. Sci. 104 36–46
[20] Zhang Y, Zhao J T, Li G, Wang Y Q, Wu K, Liu G and Sun J 2018 Alloying effects on the microstructure and mechanical properties of nanocrystalline Cu-based alloyed thin films: Miscible Cu-Ti versus immiscible Cu-Mo Acta Mater. 143 55–66
[21] Jia P, Huang R, Zhang S, Wang E and Yao J 2020 Synthesis of Ag-Cr thin film metallic glasses with enhanced sulfide–resistance J. Mater. Sci. Technol. 53 32–6
[22] Chen C, Zhang J, Duan C, Feng X and Shen Y 2016 Investigation of Cr-Al composite coatings fabricated on pure Ti substrate via mechanical alloying method: effects of Cr-Al ratio and milling time on coating, and oxidation behavior of coating J. Alloys Compd. 660 208–19
[23] Jiahong L and Dejun K 2018 Micro-structures and high-temperature friction-wear performances of laser cladded Cr-Ni coatings Materials (Basel) 11 137
[24] Wang J, Zheng K, Li L, Qi W, Zhou N and Zhao S 2011 Influence of Cr-Fe coating on wettability of aluminum on ZTA ceramics Rare Met. 30 520–3
[25] Li X Y, Akiyama E, Habazaki H, Kawashima A, Asami K and Hashimoto K 1997 Spontaneously passivated films on sputter-deposited Cr-Ti alloys in 6 M HCl solution Corros. Sci. 39 335–48
[26] Mehmood M, Akiyama E, Habazaki H, Kawashima A, Asami K and Hashimoto K 1999 The degradation of the corrosion resistance of sputter-deposited chromium–titanium alloys by nanoscale heterogeneity Corros. Sci. 41 1871–90
[27] Landolt D, Roby G and Mettraux P 1998 Microstructure and Corrosion Resistance of Sputter-Deposited Titanium–Chromium Alloy Coatings Corrosion 54 772–80
[28] Mallick B and Dearmley P A 2007 The corrosion–wear response of Cr-Ti coatings Wear 263 679–90
[29] Yu H C, Huang X Y, Lei F H, Tan X C and Han Y Y 2013 Preparation and electrochemical properties of Cr(III)-Ti-based coatings on 6063 Al alloy Surf. Coat. Technol. 218 137–41
[30] Zhang F, Li C, Yan M, He J, Yang Y and Yin F 2017 Microstructure and nanomechanical properties of co-deposited Ti-Cr films prepared by magnetron sputtering Surf. Coat. Technol. 325 636–42
[31] Xu T, Pang S, Li H and Zhang T 2013 Corrosion resistant Cr-based bulk metallic glasses with high strength and hardness J. Non-Cryst. Solids 410 20–5
[32] Zeng Z, Wang L, Chen L and Zhang J 2006 The correlation between the hardness and tribological behaviour of electropolished chromium coatings sliding against ceramic and steel counterparts Surf. Coat. Technol. 201 2282–8
[33] Tripathi P, Ramkumar J and Balani K 2019 Laser peening enhances tribological resistance of electrodeposited Cr coatings reinforced with yttria stabilized zirconia and carbon nano tubes Surf. Coat. Technol. 378 124919
[34] Lee S H and Eun S H 2011 Effect of Cr100−xTi x (x = 0–90 wt%) alloy underlayers on the high coercivity of FePt thin film below the substrate temperature of 250 °C Appl. Surf. Sci. 258 604–7
[35] Bellaiche L and Vanderbilt D 2012 The virtual crystal approximation revisited: application to dielectric and piezoelectric properties of perovskites Phys. Rev. B: Condens. Matter 85 075111–82
[36] Phasha M J, Bolokang A S and Kebede M A 2021 First-principles investigation of W-V and W-Mo alloys as potential plasma facing materials (PFMs) for nuclear application Int. J. Refract. Met. Hard Mater 95 105448
[37] Yuan X L, Xue M A, Chen W and An T Q 2014 Concentration-dependent crystal structure, elastic constants and electronic structure of ZrTi alloys under high pressure Frontiers of Physics 9 219–25
[38] Solorza-Guzmán M, Ramírez-Dámaso G, Castillo-Alvarado F L and DFT A 2021 study in bulk magnetic moment of Fe3Co1−x (0 ≤ x ≤ 1) Bull. Mater. Sci. 44 493
[39] Bouarissa N 2020 Microhardness and mechanical stability of CdSe2Te1−x 0 ≤ x ≤ 1, a pseudopotential approach Comput. Condens. Matter 22 00435
[40] Yu G, Qiao L, Dongting W, Zhang Y and Zou Y 2020 First principle calculation of the effect of Cr, Ti content on the properties of VMoNbTaWxM (M = Cr, Ti) refractory high entropy alloy Vacuum 179 104959
[41] Liao M, Yong L, Min L, Lai Z, Han T, Yang D and Intermetallics I J 2018 Alloying effect on phase stability, elastic and thermodynamic properties of Nb-Ti-V-Zr high entropy alloy Intermetallics 101 152–64
[42] Huang Z, Li Z, Wang D, Shi Y, Yan M and Fu Y 2021 Prediction of mechanical and thermo-physical properties of Nb-Ti-(V-Zr-Cr-Hf high entropy ceramics: A first principles study J. Phys. Chem. Solids 151 109859
[43] Yang J, Wang Y, Huang J H, Wang W L, Ye Z, Chen S H and Zhao Y 2018 First–principles calculations on interface structure and fracture characteristic of TiC/TiZrC nano-multilayer film based on virtual crystal approximation J. Alloys Compd. 755 211–23
[44] Forno SD and Lischner J 2019 Electron-phonon coupling and hot electron thermalization in titanium nitride Physical Review Materials 3 115203
[45] Zhao J, Liu L C, Gong H R and Gong X 2020 Cohesion strength and fracture toughness of Mo–TiC interfaces Surf. Coat. Technol. 382 125158
[46] Chen K and Bielawski M 2008 Interfacial fracture toughness of transition metal nitrides Surf. Coat. Technol. 203 598–601
[47] Wang M, Liu G, Luo X and Levchenko V A 2021 Effect of interface orientation on the adhesion strength and fracture toughness of Ni/ CrN interfaces by first-principles study Mater. Res. Express 8 096507
[48] Murray J R 1987 The Cr–Ti (chromium–titanium) system Bulletin of Alloy Phase Diagrams 2 174–81
[49] Musil J, Bell A, Vlček J and Hurkmans T 1996 Formation of high temperature phases in sputter deposited Ti-based films below 100 °C Journal of Vacuum Science & Technology A 14 2247–50

[50] Mattox D M 1989 Particle bombardment effects on thin-film deposition: A review Journal of Vacuum Science & Technology A 7 1105–14

[51] Ramanath G, Xiao H Z, Yang L C, Rockett A and Allen L H 1995 Evolution of microstructure in nanocrystalline Mo-Cu thin films during thermal annealing J. Appl. Phys. 78 2435–40

[52] Bates R J and Abu-Zeid O A 1996 Deposition of highly supersaturated metastable aluminium–molybdenum alloys by closed field unbalanced magnetron sputtering Vacuum 47 107–11

[53] Bottiger J, Karpe N, Krog J P and Ruban A V 1998 Measured and calculated thermoelastic properties of supersaturated fcc Ni(Al) and Ni(Gr) solid solutions J. Mater. Res. 13 1717–23

[54] Barna P and Adamik M 1998 Fundamental structure forming phenomena of polycrystalline films and the structure zone models Thin Solid Films 317 27–33

[55] Kang Y J, Baeg J H, Park H and Cho Y R 2020 Measurement of intrinsic hardness of deposited chromium thin films by nanoindentation method and influencing factors Korean Journal of Metals and Materials 58 207–15

[56] Harzer T P, Djaziri S, Raghavan R and Dehm G 2015 Nanostructure and mechanical behavior of metastable Cu-Cr thin films grown by molecular beam epitaxy Acta Mater. 83 318–32

[57] Tung H M, Huang J H, Tsai D G, Ai cf and Yu G P 2009 Hardness and residual stress in nanocrystalline ZrN films: effect of bias voltage and heat treatment Mater. Sci. Eng. A 500 104–8

[58] Van Swygenhoven H, Spaczér M and Caro A 1998 Role of low and high angle grain boundaries in the deformation mechanism of nanophase Ni: a molecular dynamics simulation study Nanostruct. Mater. 10 819–28

[59] Zhang P, Li S X and Zhang Z F 2011 General relationship between strength and hardness Mater. Sci. Eng. A 529 62–73

[60] Ni W, Cheng Y T, Lukitsch M, Weiner A, Lev L and Grummon D 2004 Effects of the ratio of hardness to young’s modulus on the friction and wear behavior of bilayer coatings Appl. Phys. Lett. 85 4028–30

[61] Leyland A and Matthews A 2000 On the significance of the H/E ratio in wear control: a nanocomposite coating approach to optimised tribological behaviour Wear 246 1–11

[62] Lackner J M, Major L and Kot M 2011 Microscale interpretation of tribological phenomena in Ti/TiN soft-hard multilayer coatings on soft austenite steel substrates Bull. Pol. Acad. Sci. Tech. Sci. 59 343–55

[63] Musil J, Kos Š, Ženkin Š, Ciperová Z, Javošťák D and Čerstvý R 2018 β-(Me1, Me2) and MeNx films deposited by magnetron sputtering: Novel heterostructural alloy and compound films Surf. Coat. Technol. 337 75–81

[64] Petley V, Sathishkumar S, Thulasie Raman K H, Rao G M and Chandrasekhar U 2015 Microstructural and mechanical characteristics of Ni-Cr thin films Mater. Res. Bull. 66 59–64

[65] Xu T, Pang S and Zhang T 2015 Glass formation, corrosion behavior, and mechanical properties of novel Cr-rich Cr-Fe-Mo-C-B-Y bulk metallic glasses J. Alloys Compd. 625 318–22

[66] Si J, Wang T, Wu Y D, Cai Y H, Chen X H, Wang W Y, Liu Z K and Hui X D 2015 Cr-based bulk metallic glasses with ultrahigh hardness Appl. Phys. Lett. 106 251903