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High-temperature oxidation resistance of CrAlN thin films prepared by DC reactive magnetron sputtering

Nirun WITIT-ANUN[1,2], and Adiorn BURANAWONG[1,2,*]

[1] *Materials Innovation Research Laboratory, Department of Physics, Faculty of Science, Burapha University, Chonburi, 20130, Thailand*
[2] *Thailand Center of Excellence in Physics (ThEP), MHESI, 10400, Bangkok, Thailand*

***Corresponding author e-mail:** adisornb@buu.ac.th

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Abstract

CrAlN thin films were prepared by using the reactive DC unbalanced magnetron sputtering method from the single alloy target on a silicon substrate. The effect of annealing temperature in the air which ranges from 500°C to 900°C for 1 h on phase structure, film composition, surface morphology, microstructure, and hardness was investigated by XRD, EDS, FE-SEM, and Nanoindentation techniques, respectively. The high-temperature (up to 900°C) oxidation resistance of the thin film was also evaluated. The result shows that solid solutions of (Cr,Al)N with (111), (200), and (220) planes for the as-deposited film and no oxide phase were found after annealing with different temperatures. The O content slightly increases with an increase in the annealing temperature with various Cr, Al, and N contents found by the EDS. From the FE-SEM result, as increased annealing temperature, the evolution of cross-sectional morphology from dense to compact columnar structure was exhibited but the oxides layer was not detected. These results concluded that the as-deposited thin film showed good oxidation resistance when annealed in air at an elevated temperature reaching 900°C. Moreover, the film's hardness decreased from 61.19 GPa to 50.11 GPa with increasing the annealing temperature observed by the Nanoindentation technique.

1. Introduction

Nowadays, surface engineering technologies fields mainly surface treatment or surface coating on machining materials have been introduced to various hard coating industries and research areas not only to achieve the desired properties but also and extend the lifetime and performance of tooling [1,2]. Currently, the Physical Vapor Deposition (PVD) coating techniques are available for a variety of applications in many areas such as optical coating to ensure high transmission or anti reflections of workpieces [3], for decorative coating purposes due to the shiny, metallic-like, and beautiful color appearance on the surface of material surface [4] and hard coating for, gears, and cutting and forming tools [5,6] have been successfully employed as wear resistant against abrasion during operated which prolongs the service lifetime.

A hard coating is currently a standard processing step deposited by the transition nitride compound thin film in the tool industry. The first generation of PVD hard coating was titanium nitride (TiN) coatings which received extensive and close attention due to their extreme hardness, excellent wear resistance, high corrosion resistance, and high melting point [7]. Due to the development of a dense oxidation film, chromium nitride (CrN) thin film performs superior oxidation resistance compared to TiN thin film during elevated temperatures environment. However, CrN is unable to keep up with demand because of the harsher working conditions [8] and has some limitations with respect to deterioration at high temperatures (>600°C) because the films reacted with oxygen from the atmosphere and oxidized to form oxide compounds in the film. These results affected the structure and mechanical properties or may cause the films to peel off from the substrate. Finally, the service lifetime of tooling was reduced [9].

The way to solve the problem of thin film deterioration can be done by incorporating of Al atoms into the cubic CrN crystalline structure forming a ternary nitride chromium aluminum nitride (CrAlN) thin films, which exhibited better oxidation resistance than CrN thin film [10]. High thermal stability and oxidation resistance are essential considerations and hence required properties because they are often exposed to air ambiance at elevated temperatures [11]. From the previous study, Li *et al.* [9] deposited CrAlN thin film by closed field unbalanced magnetron sputtering and performed high-temperature resistance up to 800°C and extremely high hardness up to 48 GPa due to the formation of complex oxides of Cr_2O_3 and Al_2O_3 in the film structure which eventually suppresses oxygen diffusion into the bulk [12]. It was confirmed that the aluminum in the structure of the CrN can enhance the hardness and oxidation resistance properties at elevated temperatures. Therefore, the CrAlN thin film is the great interest for many engineering applications that require protective coatings because of their potential unique properties [13-15].

The CrAlN thin films were commonly prepared by the PVD technique as reactive magnetron sputtering methods can be carried from various types of targets such as co-target, mosaic target, or alloy target. These targets have their advantages and drawbacks [16]. The use

of the alloy target to produce thin film offers some advantages such as easily adjustable compositions and process simplification [17]. Most previous researchers reported the preparation and characterization of the CrAlN thin film co-target sputtering method as well as the oxidation resistance through the annealing temperatures [10-16] but much fewer reports are available in the literature on the high temperatures oxidation resistance of the film deposited using alloy target. It may partly be attributed to the difficulty in preparing dense CrAlN films. Hence, more detailed studies including the oxidation resistance, and the relation between crystal structure, surface morphology, and microstructure under various oxidizing conditions in the detail are still needed.

The aim of this study is to understand and discuss the oxidation behavior of CrAlN coatings deposited by the DC Reactive Magnetron Sputtering technique using an alloy target. The influences of annealing temperature (up to 900°C) on phase structure, film composition, surface morphology and microstructure, and hardness were investigated. Also, the high-temperature oxidation resistance of these films was presented as well in this paper.

2. Experimental

The chromium aluminum nitride (CrAlN) thin films were prepared on a Si substrate by a reactive DC unbalanced magnetron sputtering from a homemade vacuum coating system (Figure 1). The cylindrical stainless-steel coating chamber had a diameter of 31.0 cm, a height of 31.0 cm, and a water-cooled cathode was mounted on the top of the coating chamber. The cathode was an unbalanced magnetron cathode achieved by installing magnets of different intensities as 1800 G strength in the center of the cathode and 1300 G on the sides of the cathode. The coating target used is an alloy of chromium-aluminum alloy (50 at% Cr/50 at% Al) a disc type with a diameter of 5.0 cm and a thickness of 3.0 mm was used as a sputtering target. A 1000 V with 3 A DC high voltage was equipped as a power supply for a vacuum coating system. The chamber was connected to the pump system which consisted of a diffusion pump and a rotary pump. The pressure measurement in the coating chamber was carried out using the pressure measurement system of PFEIFFER, which uses the display model TPG262 and the pressure gauge of the Compact Full Range Gauge, model PKR251. There are two types of gas used in the coating, namely argon gas (99.999%) gas was sputter gas and nitrogen gas (99.995%) was reactive gas. Both gases are supplied to the coating chamber through the control of the MKS type247D mass flow regulator.

The thin film preparation process starts with installed by placing 10.0 cm away from the coating target, then create a vacuum condition by reducing the pressure inside the coating room until the base pressure was 5.0×10^{-5} mbar and then releasing the gas into the coating chamber. The argon gas and nitrogen gas flow rates were fixed throughout the coating at 20.0 sccm and 6.0 sccm respectively. During the film preparation, the pressure was kept constant at 5.0×10^{-3} mbar by adjusting the high vacuum valve. Each film was coated for 30 min. The conditions for thin film coating are summarized in Table 1.

All the thin films prepared in this research were characterized by various techniques. The crystal structure was studied by the grazing incident X-ray diffraction (GIXRD: Bruker's D8 ADVANCE), which was a 2θ-scan measurement with a grazing incident angle of 2°.

Table 1. Deposition conditions of CrAlN thin film.

Parameters	Details
Target	Alloy of Cr and Al
Base pressure	5.0×10^{-5} mbar
Working pressure	5.0×10^{-3} mbar
Argon to Nitrogen gas flow rate	20:6 sccm
Sputtering power	226 W
Target to substrate distance	10 cm
Deposition time	30 min

The diffraction patterns were collected as 2θ angles from 20° and 80°. The crystal size was calculated using Scherrer's equation from the X-ray diffraction pattern of the film. The microstructure, cross-sectional morphologies, and thickness were investigated using a Field Emission Scanning Electron Microscopy (FE-SEM: Hitachi s4700). The element compositions of the films were measured using Energy Dispersive X-ray Spectroscopy (EDS: LEO 1450VP) technique attached to a Scanning Electron Microscope (SEM: EDAX's).

The oxidation resistance of the films was evaluated by annealing in the air from 500°C to 900°C with an increment step of 100°C for each sample. The annealing time was kept constant of 1 h. The as-deposited films were placed into a crucible and annealed in an electric furnace (CARBOLITE CWF1300) and then cooled in air. After the annealing step, the oxidation resistance of samples was evaluated by means of GIXRD, EDS, and FE-SEM techniques, respectively.

The nanohardness values of the CrAlN thin films were investigated with a nanoindenter (Micromaterial - NanoTest) equipped with a Berkovich diamond probe tip. The tests were performed with a constant indentation depth not more than 10% of film thickness to avoid the substrate effect. Nine indentation tests were conducted for each film.

3. Results and discussion

3.1 Phase structure of the CrAlN thin films

The crystal structure of the thin films coated in this study before and after annealing at temperatures in the range of 500°C to 900°C for 1 h was obtained. The X-ray diffraction patterns were obtained by GIXRD analysis as shown in Figure 1, but because chromium aluminum nitride has a solid solution structure which does not have a JCPDS standard structure. In this case, there is no standard data in the database for comparison and reference. The standard X-ray diffraction pattern angles of chromium nitride (JCPDS No.65-2899) and aluminum nitride (JCPDS No.88-2250) were added data indicating for reference and comparison. The results revealed that the films exhibited X-ray diffraction patterns at 2θ of 37.50°, 43.59°, and 63.63° which are located between the diffraction angles of chromium nitride (CrN) and aluminum nitride (AlN) at the (111), (200) and (220) planes without X-ray diffraction patterns of chromium nitride compounds and aluminum nitride were exhibited.

The results from the GIXRD technique indicated that the as-deposited thin film in this work was a solid solution of (Cr,Al)N with a crystal structure of FCC formed by the substitution of smaller atoms of aluminum (atomic radius is 0.121 nm) into chromium atom (atomic radius is 0.139 nm) in the chromium nitride crystal structure [9].

Moreover, the lattice constant of 4.150 Å, which is between the standard lattice constant of aluminum nitride (3.938 Å) and chromium nitride. (4.148 Å), thus the angle of the x-ray diffraction pattern of the film was shifted to higher 2θ values compared to the diffraction angle of chromium nitride [18]. This result was also confirmed that the as-deposited films were solid solutions.

The X-ray diffraction patterns of CrAlN thin films which were annealed in air at temperatures in the range of 500°C to 900°C for 1 h were analyzed by the GIXRD technique and shown in Figure 1. The 2θ X-ray diffraction patterns of 37.80° to 37.93°, 43.95° to 44.06°, and 63.92° to 64.07° which correspond to (111) (200) and (220) planes of solid solution CrAlN thin film were investigated. From these results, there was no difference in diffraction pattern between annealed and the as-deposited thin film. The intensity of the X-ray diffraction pattern of the annealed film changes according to the increasing annealing temperature. At 500°C, the intensity of the X-ray diffraction pattern was increased for all planes. In this case, the film was crystalline. It was attributed to the annealing process directly giving high enough energy to atoms in the film causing the condense and rearrange of the crystals which is called "recrystallize". Therefore, the intensity of the X-ray diffraction pattern was increased [19]. As the annealing temperature increased from 600°C to 900°C, the intensity of the X-ray diffraction pattern for all three planes was still observed. On the other hand, the X-ray intensity continued to decline at the (220) plane and the intensity of the X-ray diffraction at the (220) plane almost disappeared. It was due to energy from the annealing process helps the film to be denser.

The decrease of film thickness from 1136.5 nm to 1077.0 nm (Table 2) which measured from FE-SEM also affected the intensity of the X-ray diffraction patterns of the film at various annealing temperatures. It may also be the fact that some of the chromium or aluminum atoms in the film react with oxygen in the atmosphere forming oxides of amorphous structure but in small quantities, because the X-ray diffraction pattern was not observed for both chromium oxide and aluminum oxide compounds. The intensity of the X-ray diffraction pattern of the film at temperatures in the 600°C to 900°C range was reduced. The results of this section show that the as-deposited CrAlN thin films in this research were performed thermal oxidation at high temperatures up to 900°C, which good agreement with the result from Li *et al*. 2012, which found that chromium aluminum nitride films can perform high temperatures oxidation resistance of up to 800°C due to the formation of complex oxides of Cr_2O_3 and Al_2O_3 in the crystal structure of the film [9].

The crystal size of CrAlN thin film calculated from Scherrer's Equation [20] was shown in Table 2. It was found that the as-deposited thin film had a nanometer structure. Since the crystal size of all planes of the film was less than 25 nm, it was also found that the crystal size of the film increased with increasing annealing temperature at all planes. At the (111) plane, the crystal size increased from 19.1 nm to 20.9. nm was investigated, increased from 15.6 nm to 23.8 nm and 15.6 nm to 22.33 nm the (200) and (220) planes were also found, respectively. It was found that the average crystal size was increased from 17.2 nm to 22.4 nm with the annealing temperature because the heat energy in the annealing process caused This result can be explained that the thermal energy produced by annealing leads to enhancement of mobility of active sites. The increase of mobility can be attributed to grain growth [21], therefore, the crystal size increases with the annealing temperature.

The lattice constant of the as-deposited and annealed CrAlN thin films at different annealing temperatures is summarized as shown in Table 2. The results showed that the film had a lattice constant in the range of 4.104 Å to 4.150 Å. At the (111) plane, the lattice constant was varied between 4.104 Å to 4.150 Å, the planes (200) and (220) were in the ranges of 4.106 Å to 4.148 Å and 4.106 Å to 4.132 Å, respectively, which were found to remain between the standard value of aluminum lattice (3.938 Å) and chromium (4.148 Å). This evidence can conclude that the annealing temperature of the CrAlN thin films deposited by DC reactive magnetron sputtering in this research did not affect or alter the structure of the as-deposited thin films or did not induce the structure of the oxide layer after the annealing process, indicating that the thin film is oxidation resistant at temperatures up to 900°C.

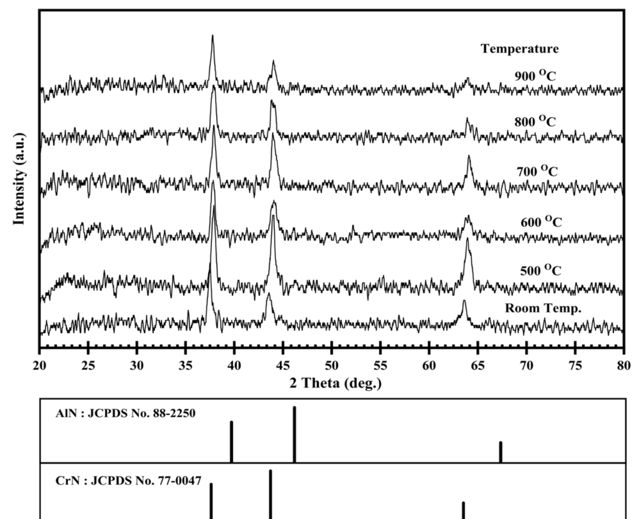

Figure 1. XRD patterns of CrAlN thin film at various annealing temperatures.

Table 2. Thickness, crystal size, and lattice constant of CrAlN thin film at various annealing temperatures.

Annealing Temperature (°C)	Thickness (nm)	Crystal size (nm)				Lattice constant (Å)		
		(111)	(200)	(220)	average	(111)	(200)	(220)
RT	1114.0	19.1	15.6	17.0	17.2	4.150	4.148	4.132
500	1136.5	19.1	17.1	15.6	17.3	4.111	4.115	4.109
600	1129.5	19.1	16.5	16.4	17.3	4.113	4.106	4.110
700	1035.0	19.5	17.9	17.7	18.4	4.107	4.107	4.106
800	1084.0	19.5	16.2	21.8	19.2	4.104	4.111	4.110
900	1077.0	20.9	23.8	22.3	22.4	4.117	4.107	4.109

3.2 Morphology of CrAlN thin films

Figure 2 shows the FE-SEM surface morphology investigation of CrAlN thin films as a function of annealing temperature. It was found that the surface of all thin films did not change through the annealing temperature. The as-deposited (Figure 3(a)) has a smooth surface. The small fine grain is distributed over the surface of the film. When the film was annealed in the range of 500°C to 900°C, almost no change of grain on the film surface was observed which the grain of the film is still the same pattern with small and finely distributed as shown in Figure 2(b-f). This result can be concluded that the film was performed oxidation resistance due to its dense structure which also supports the result from XRD results

This result can be supported by the oxidation behavior from previous literatures [22], It was found that the significantly change of grain evolution with more grain aggregation accompany with more void between grains was obviously observed when the film was oxidized at a given annealing temperature. However, the grain still unchanged was obtained from this study. It can conclude that the surface morphology did not change through the annealing temperature. Therefore, the film was showed oxidation resistance reaching to 900°C.

Regarding the cross-section investigation of CrAlN thin films annealed at different annealing temperatures could be verified by the FE-SEM micrograph (Figure 3). It was found that the structure of the film changes with increasing annealing temperature. The as-deposited thin film at room temperature without annealing (Figure 4(a)) and the film annealed at 500°C (Figure 3(b)) were found to be similar cross-sectional morphology which is unstructured. When the annealed at 600°C the film structure changed, which was dense. There is no void between the grains, which also corresponds to Zone T [23] (Figure 3(c)). Moreover, it was found that the film structure was clearly changed to a columnar type with compact characteristics and exhibited a void between each grain (Figure 3(d-f). The cross-section morphology of the thin film corresponds to Zone 2 (Figure 3(d-f), according to Thornton's Zone structure model [23] was found for the film annealed in the air at various temperatures ranging from 700°C to 900°C.

In the case of the oxidation behavior of thin film, the oxide layer which was a separated layer on the as deposited thin film after annealing with difference temperatures. This result was also good agreement with the XRD and surface morphology investigation. It can confirm the high temperature resistance reaching to 900°C obtained from this research.

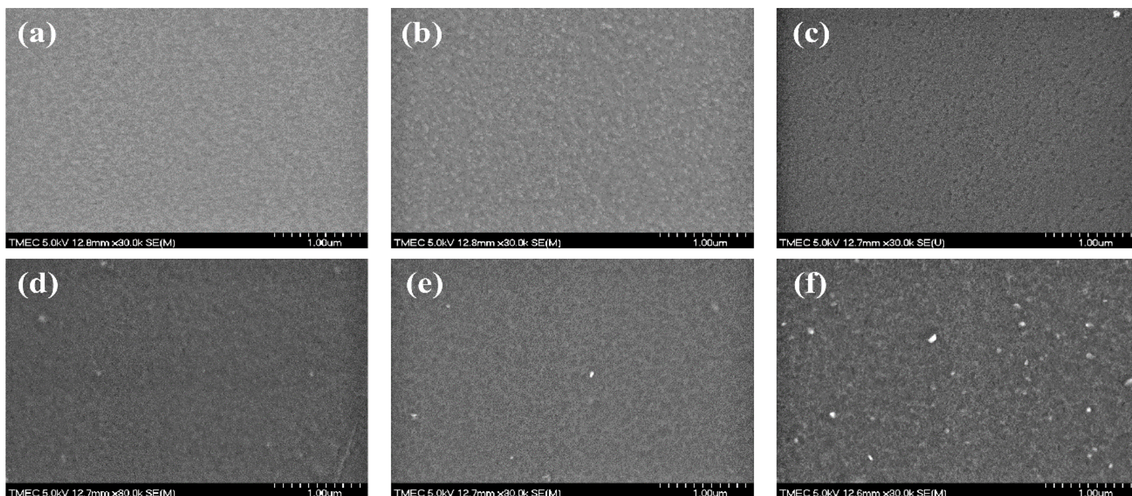

Figure 2. Surface morphology of CrAlN thin film at various annealing temperatures (a) room temp., (b) 500°C, (c) 600°C, (d) 700°C, (e) 800°C, and (f) 900°C.

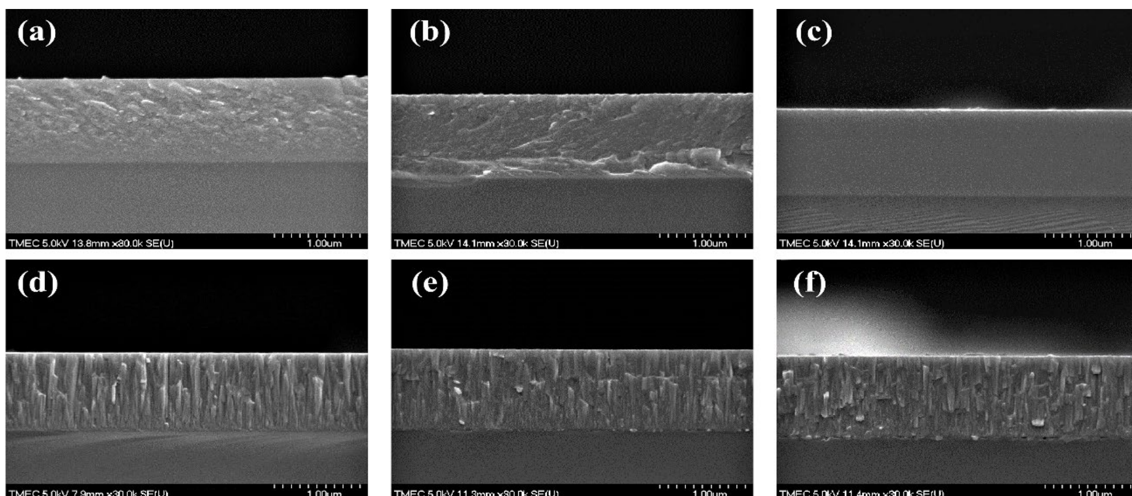

Figure 3. FE- SEM cross-sections of CrAlN thin film at various annealing temperatures (a) room temp., (b) 500°C, (c) 600°C, (d) 700°C, (e) 800°C, and (f) 900°C.

3.3 Chemical compositions of CrAlN thin films

Table 3 showed the chemical composition of CrAlN thin films before and after annealing at different temperatures. The EDS analysis revealed that the thin films obtained in this research before annealing contained Chromium (Cr), Aluminum (Al), and Nitrogen (N) content with various quantities. The chromium content of 10.21 at%, aluminum of 19.97 at%, and nitrogen of 53.81 at%, and a small fraction of oxygen (O) were found to be approximately 16.02 at% for the as-deposited thin film. When the film was annealed in the air from 500°C to 900°C for 1 h, it was found that the chemical composition of the film was slightly changed. The Cr, Al, and N contents decreased from 10.14 at% to 9.60 at%, 19.95 at% to 18.14 at%, and 53.82 at% to 49.32 at%, respectively, whereas oxygen content increased from 16.02 at% to 22.94 at%, which is slightly increased.

The oxygen content in the film being approximately 16.02 at% was identified for the as-deposited film. It was maybe that the residual oxygen inside the coating chamber has existed although the base pressure before the coating is very low at 5.0×10^{-5} mbar. However, there was a small increase in oxygen content approximately 6 at% in the film after the annealing temperature reached up to 900°C. It was an interesting point and good agreement with the results from GIXRD that no X-ray diffraction patterns of oxide compounds containing Cr_2O_3 and Al_2O_3 were detected. As a result of the annealing process, a heat from high annealing temperatures could allow diffusion of oxygen into the film structure with the oxygen content of approximately 22.94 at% was investigated from the EDS technique.

A similar kind of result was also observed by Khamseh *et al*. [15] who studied the oxidation resistance properties of chromium aluminum nitride thin films when annealed the film at different temperatures in the range of 700°C to 1000°C. The oxidation resistance was exhibited at annealing temperatures up to 900°C. The film was oxidized at 1000°C with chromium and aluminum oxide compounds obtained from the XRD technique. In addition, the oxygen content was increased to 64.1 at% as a function of annealing temperature [15] but the results of this work showed that the oxygen content in the film was only 22.94 at% as a slightly increase of approximately 6 at% from annealing was obtained when annealed at 900°C. It can conclude the result from the EDS technique were also confirmed that the CrAlN thin film which prepared in this research performed oxidation resistance up to 900°C and also support the GI-XRD investigation that oxide compound structure cannot be detected. It was due to the oxygen may cannot forming an oxide compound or may form as an amorphous oxide compound which cannot be founded from the XRD diffraction patterns.

3.4 Hardness of the CrAlN thin films

The hardness value as a function of annealing temperature was shown in a Figure 4. The hardness of the as-deposited thin film was 67.19 GPa. At the annealing temperature of 500°C, the hardness value was slightly decreased to 66.55 GPa. The increase of hardness value to 69.76 GPa was obtained for the annealing temperature of 600°C. When the annealing temperature increased to 700°C, the hardness value was decreased to 65.76 GPa. As the annealing temperature increased from 800°C to 900°C, the hardness values were significant decreased to 57.11 and 50.11 GPa, respectively, when annealed for 1 h.

The relationship between hardness value and cross-sectional morphology from FE-SEM technique through the annealing temperature was also investigated. The unstructured morphology was found for the as-deposited thin film which has a hardness value of 67.19 GPa. When increase annealing temperature to 500°C, the dense structure resulting in the highest hardness value of 69.76 GPa was founded. The lowest hardness value (50.11 GPa) was observed due to the cross-sectional structure was changed to the columnar structure which has a void between grain boundaries. This result can conclude that the annealing temperature was directly affected to the evolution of the cross-sectional structure resulting in the decreased of hardness value.

Figure 5 showed the comparison of hardness value with oxygen content through the difference in annealing temperature. It was found that not only the annealing temperature affected to oxygen content but also influenced the hardness value of the thin film. When increased annealing temperature was to observe the oxidation behavior of the thin film, the increase of oxygen content from 15.74 at% to 22.94 at% whereas the decreased of hardness value from 67.19 GPa to 50.11 GPa was identified, respectively. Although the incorporate of oxygen content in the film structure resulting the decrease of hardness value when annealed at a high temperature reaching to 900°C, the high hardness value of the film in the range of 50.11 GPa to 67.19 GPa was obtained. It can conclude that the films were super hard coating properties (hardness value > 40 GPa) during the annealing process [24]. The results were well supported by the GIXRD EDS and FE-SEM results which indicated that the good oxidation resistance and high hardness stability at high up to 900°C. The as-deposited films were also good candidates for high-temperature applications.

Tables 3. Chemical composition of CrAlN thin film at various annealing temperatures.

Annealing temperature	Composition (at%)			
(°C)	Cr	Al	N	O
R.T.	10.21	19.97	53.81	16.02
500	10.14	19.95	53.82	16.09
600	10.23	19.95	52.47	17.35
700	10.13	19.54	52.76	17.57
800	9.89	19.45	50.54	20.12
900	9.60	18.14	49.32	22.94

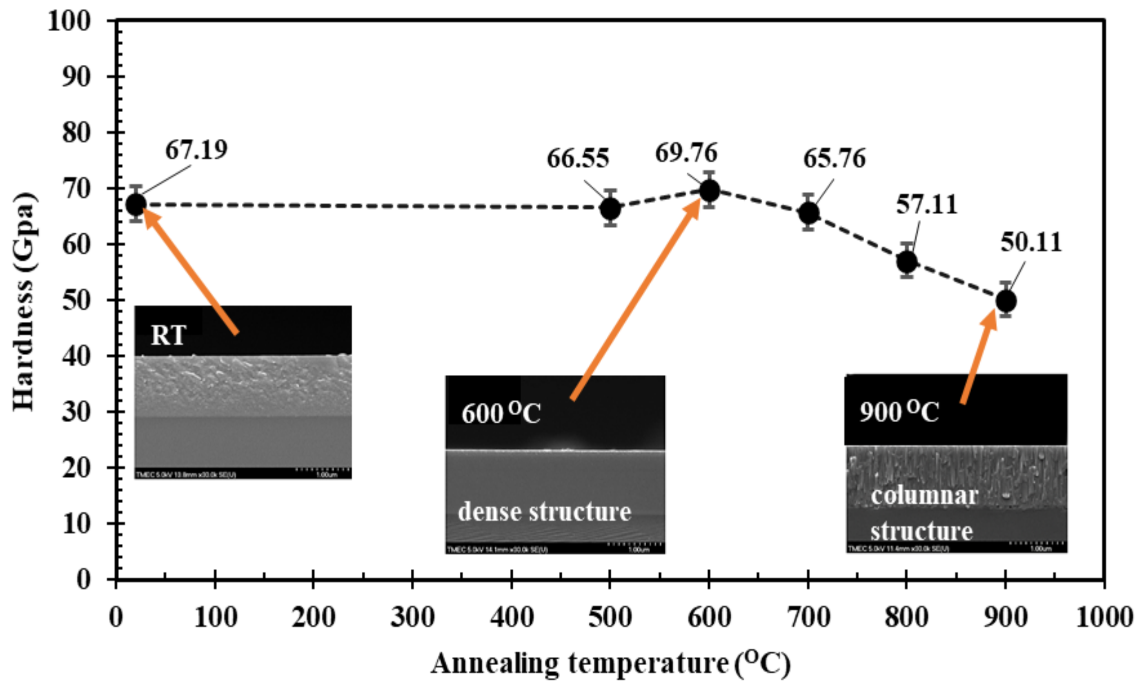

Figure 4. Hardness of CrAlN thin film at various annealing temperatures.

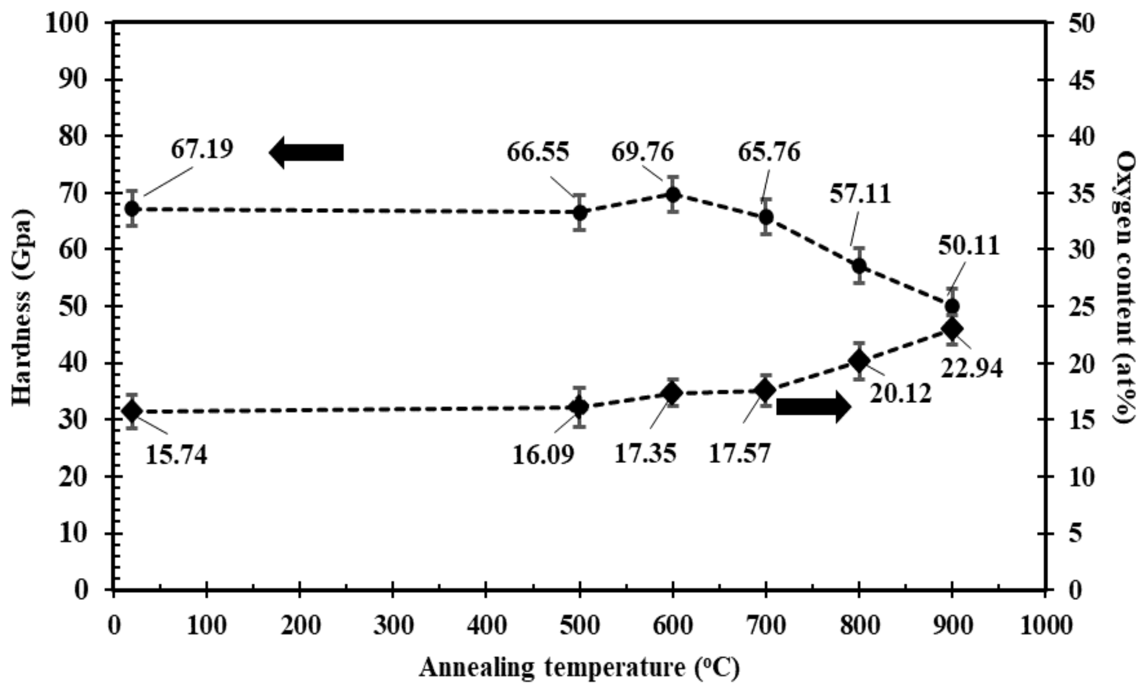

Figure 5. Hardness vs O content of CrAlN thin film at various annealing temperatures.

4. Conclusion

In this study, CrAlN thin films on Si substrate by reactive DC unbalanced magnetron sputtering techniques from Cr-Al alloy coating targets at room temperature without additional heating or bias. The results showed that the thin film coated at room temperature was a solid solution of (Cr,Al)N at the (111), (200), and (220) planes with crystal size and lattice constant of the film were in the range of 15.6 nm to 19.1 nm and 4.104 Å to 4.150 Å, respectively. The Cr, Al, and N elements were investigated in different ratios with a small amount of oxygen. However, when the film was annealed in the air for 1 h from 500°C to 900°C, the crystallinity of the film was changed according to the annealing temperature. Furthermore, diffraction patterns of both chromium and aluminum oxide compounds were not observed. The film was increased crystallinity as annealed reached to 500°C. When the annealing temperature is increased to 600°C to 900°C, the crystallinity of the films was decreased. The average crystal size of the film increased from 17.2 nm to 22.4 nm as the annealing temperature increased. The results of microstructural studies from the FE-SEM technique showed that the film obtained

at low temperatures had a dense structure and converted to columnar at temperatures above 700°C. The film was changed according to the temperature and found that the Cr Al and N content has a slight decrease while the O content increased slightly with increasing temperature. It was also found that when the annealing temperature was raised up to 900°C, the O content in the film increased only slightly. Neither the crystal structure nor any oxide layers of chromium and aluminum were found. The results of this study, therefore, show that annealing of chromium aluminum nitride thin films at different temperatures has little effect on the film structure and morphology. It can conclude that the CrAlN thin films in this study obtained by adding aluminum to the chromium nitride structure show excellent oxidation resistance up to 900°C. The film's hardness decreased from 67.5 GPa to 50.1 GPa was obtained for the nanoindentation technique. The as-deposited films were likewise suitable for high-temperature applications for tooling.

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