Thermal Stability of Arc Evaporated ZrCrAlN

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Abstract
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Keywords
Thermal Stability, ZrCrAlN, Reactive Cathodic Arc Evaporation, Anneal, Age Hardening, XRD, EDS, Nanoindentation, Hardness.
Abstract

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1. Introduction

1.1 Background

Coatings have multifarious applications in today’s world. The gamut of applications includes decorative coatings like coatings on watches, electrically conductive coatings as the ones used for electrical contacts, the protective coatings such as hard coatings on tools to reduce wear etc.

The industrial demand for higher turning speeds exposes the hard coatings to extreme conditions of high temperature and high pressure during the cutting operations. Only those coatings which show thermal stability are suitable candidates under these rugged conditions. Ternary Nitride coatings such as TiAlN and CrAlN have long established reputation as the preferred choice for hard coatings on cutting tools. TiAlN and ZrAlN coatings exhibit significant age hardening when annealed at higher temperatures and have good resistance to oxidation. CrAlN coatings show weak age hardening and exhibit extremely good oxidation resistance. The age hardening in TiAlN coatings is caused by the formation of coherent cubic TiN and AlN rich domains during spinodal decomposition [1]. The age hardening in ZrAlN is ascribed to the nucleation and growth of nanocrystalline cubic ZrAlN surrounded by an amorphous phase [2]. In the case of CrAlN the age hardening is observed for low temperatures due to AlN precipitation close to grain boundaries [3]. However as both Al and
Cr form good protective oxides suppressing further oxygen diffusion these coatings offer better oxidation resistance comared to TiAlN [4].

Recently the research in multinary nitride coatings has shown improved wear resistance as well as better oxidation resistance under high temperatures as compared to the ternary nitride coatings. This opens a new vista into the research of multinary coatings. TiCrAlN has already shown better wear resistance than TiAlN and CrAlN [5]. Similarly ZrCrAlN is also an auspicious candidate which needs to be explored.

1.2 Objectives

The purpose of this thesis is to explore the thermal stability of the ZrCrAlN material system. This is carried out by depositing fourteen different compositions of ZrCrAlN coatings onto WC-Co substrates with reactive cathodic arc evaporation. The annealing of these samples is then carried out at a temperature range of 800 °C-1100 °C with an increment of 100 °C. The compositions of the coatings were established by EDS. XRD is used to determine the crystal structure of the coatings and nanoindentation is done to determine the hardness of these coatings.
2. Theory

2.1 Metal Cutting

To harness the benefits offered by metals, they need to be cut and shaped. To cut and shape the metals, tools are required. The ideal tool material should have the following properties:

- Harder than the work piece.
- High Toughness.
- Chemically inert to the work piece.
- Can withstand thermal shocks.

Cemented Carbide is the material that strikes a good balance among the above mentioned properties as shown in fig1.
2.1.1 Cemented Carbide

Cemented Carbide is a marvel of powder metallurgy. It consists of hard carbide particles which are cemented together by a binder [7]. Tungsten Carbide (WC), Titanium Carbide (TiC), Tantalum Carbide (TaC) and Niobium Carbide (NbC) are the commonly used hard carbide particles whereas the common binders are Cobalt (Co) and Nickel (Ni).

Due to the unique combination of hardness and Toughness of cemented carbide tools they have a broad application range and can be used for machining of most work piece materials. However with a coating the cutting speed and the tool life time can be drastically increased.

2.2 Thin Film Deposition Techniques

The methods of thin film deposition can be broadly divided into two categories, chemical vapour deposition (CVD) and physical vapour deposition (PVD). Both methods have unique advantages. In this work, a PVD method called Cathodic Arc Evaporation is used.
2.2.1 Chemical Vapour Deposition

Chemical vapour deposition, as the name suggests, is the process involving chemical reactions. In CVD the coating materials are introduced in the chamber in gaseous phases which chemically react to form the desired composition of the coating on the heated substrate. The advantage of the material being in a gaseous phase is that the complex shapes can be coated easily.

In conventional CVD the deposition of coatings is carried out at temperatures greater than 1000 °C. Decarbonisation of cemented carbide is catalysed at such a high temperature which leads to the decrease in toughness of the tool. [8]. Due to the involvement of high temperatures during the CVD processes it is difficult to deposit coatings in metastable state.

2.2.2 Physical Vapour Deposition

In conventional physical vapour deposition processes, the physical processes like evaporation and condensation are involved for the deposition of the film onto the substrate. The deposition process can be carried out at room temperature. This gives it an edge over the CVD for the deposition of metastable coatings. There are several PVD techniques for deposition of hard coatings like magnetron sputtering and cathodic arc evaporation.

2.2.2.1 Cathodic Arc Evaporation

In this technique the cathode which is made of the material to be deposited is struck by a high current and low voltage arc. This high current and low voltage discharge melts the cathode surface locally and this localized point is referred to as the cathode spot [9]. From this cathode spot the molten material is vaporized into plasma which is transported to the substrate. The cathode spot is only active for 10 ns-1µs and leaves a crater on the cathode
surface [10]. After this short time another spot appears randomly on the cathode surface. The whole arc process is thus self-sustaining. Magnetic field is used to steer the arc for the uniform erosion of the cathode.

Schematics of the cathodic arc evaporation system and the process are shown in fig.2 and fig.3.
Figure 3. Cathodic Arc Evaporation Process (after [11]).
3. Material Systems

The earliest material system of ceramic coatings for cutting tools was TiN. TiN improves the cutting performance of cutting tools [12]. However TiN has limited stability at elevated temperatures. Oxidation of these coatings is initiated around 600 °C [13]. Al was then added to this system which resulted in improved high temperature properties [14]. The new material system TiAlN showed superior oxidation resistance and better machining performance [14]. This motivated to study other binary metal nitride systems with the addition of aluminium. The new ternary metal aluminium nitride systems e.g. CrAlN [15], ZrAlN [16], ScAlN[17] and HfAlN[18] showed better results than their parent binary nitride systems.

CrAlN shows better oxidation resistance than TiAlN [19] whereas TiAlN system exhibit age hardening with improved high temperatue mechanical properties [1]. Thus the researchers attempted to blend these material systems in order to culminate the benefits of both systems into one system. This has taken the research into the domain of multinary nitride systems. The new material system TiCrAlN proved better than TiAlN and CrAlN [5, 20].
ZrAlN is an underexplored material system which has shown significant age hardening with a hardness increase of 36% compared to its as deposited state [2]. The mixing of this system with CrAlN yields a new multinary nitride ZrCrAlN which needs to be investigated. In this chapter material systems related to ZrCrAlN systems are discussed. In ZrCrAlN system cZrN has the lattice parameter of 4.577Å, the lattice parameter of cCrN is 4.14Å and the lattice parameter of cAlN is 4.07Å.

3.1 Binary Nitride Systems

3.1.1 Zr-N System

Like TiN coatings, ZrN coatings are also yellow in colour but are brighter. The most stable crystal structure for ZrN compound is the NaCl structure, as shown in fig 4(i), with a lattice parameter of \(a = 4.58\)Å [21]. The hardness of arc evaporated ZrN coatings is reported to be in the range of 21-27 GPa [22,23]. It is similar to TiN in terms of hardness [24] and oxidation resistance [25].

\[\text{Figure 4. (i) NaCl structure and (ii) Wurtzite structure.}\]
3.1.2 Cr-N System

CrN coatings have a metallic silver colour. The crystal structure of these coatings depends upon the deposition conditions. The metastable crystal structure of CrN coatings is NaCl structure, as shown in fig4(i), with a lattice constant of \( a = 4.14 \text{Å} \) [26]. CrN coatings also exhibit a stable wurtzite structure as shown in fig4(ii), depending on the growth conditions [27], with lattice parameters of \( a = 4.81 \text{Å} \) [28] and \( c = 4.48 \text{Å} \) [28]. CrN coatings offer better oxidation resistance than TiN [29]. As the crystal structure in these films strongly depend on the deposition conditions so is the hardness [30]. These coatings show hardness in a broad range of 12-30GPa [30].

3.1.3 Al-N System

AlN primarily has recognition as a wide band gap semiconductor material for electronic applications and is not used as a hard protective coating. The Wurtzite structure, shown in fig.4(ii), is the equilibrium structure of this material with lattice parameters \( a = 3.11 \text{Å} \) [31] and \( c = 4.98 \text{Å} \) [31]. Besides wurtzite structure it can also exist in metastable state as a cubic NaCl structure, shown in fig. 4(i), with lattice constant of \( a = 4.05 \text{Å} \) [32].

3.2 Ternary Systems of Nitrides

3.2.1 Zr-Al-N System

Theoretical studies have shown that ZrAlN exhibits a higher miscibility gap than TiAlN and CrAlN [33]. It has been shown that for \( x \leq 0.36 \) at. % in \( Zr_{1-x}Al_xN \), i.e. low Al content, the cubic phase is stable [34]. For \( x > 0.70 \) at %, i.e. high Al content, hexagonal structure is
promoted [34]. Whereas for intermediate Al contents a mixture of cubic, hexagonal and amorphous structure exists [34].

3.2.2 Cr-Al-N System

CrAlN coatings are used for high temperature oxidation resistance applications. CrAlN films can be obtained in a wide range of compositions due to the high solubility of CrN in AlN [35]. Its crystal structure is shown to have a cubic NaCl structure in the range of $x = 60-70$ at.% [36]. For $x$ ranging from 70 at.% to 83 at. % the structure is a mixture of cubic and wurtzite [36]. For $x > 83$ at.% the structure completely transforms to wurtzite during the deposition [36]. Coatings with cubic (NaCl) structure have shown age around 700 °C. As soon as the temperature increases beyond 900 °C the structure transforms to hexagonal, i.e. wurtzite, and the mechanical properties depreciate [37]. The as-deposited value for these coatings is ~30GPa [38]. The coatings with a cubic structure have shown superior oxidation resistance due to the formation of complex oxides at elevated temperatures [37].
4. Analysis Techniques

Different combinations of techniques have been employed for the analysis of the coatings. The techniques provide valuable information regarding chemical composition, microstructure and mechanical properties.

4.1 Energy Dispersive X-ray Spectrometry (EDS)

EDS relies on X-ray spectrum emitted by a sample as it is being bombarded with a focused electron beam to obtain a localized chemical analysis. Elements from atomic number 4(Be) to 92(U) can be detected with this technique. The depth resolution of this technique is 0.3-5µm.

The process involves a focused beam of highly energetic electrons, in the range of keV, incident on the specimen. The different species that can be witnessed besides X-rays as the sample is bombarded with an electron beam are shown in fig 6. This incident beam of electron may knock out an electron from the inner shell of atom within the sample and thus creating a hole as shown in fig 5. An electron from the outer shell then fills this hole. The difference in energy between the outer shell and the inner shell can be released as X-rays. The emitted X-ray photon is then registered by the energy dispersive spectrometer. Since
each element has a unique atomic structure the emitted energy of the X-rays are unique for each element. This provides detection of the elemental composition of the coatings.

Figure 5. Generation of X-rays from an atom

Figure 6. Generation of Different Species from the Sample under Energetic Electron Beam
4.2 X-ray Diffraction (XRD)

X-ray Diffraction has multiple uses in relation to the investigation of the material at hand. The most common of the uses include measurement of average spacing between the rows or layers of atoms, determination of the orientation of single crystals or grains, to determine the crystal structure of an unknown material, grain size measurements, shape and internal stress of a small crystalline regions etc. The advantages of using this technique are that it is non-destructive and the sample preparation is very convenient.

As the name implies, this method is based on the diffraction of X-rays. The process involves an incident X-ray beam on the material which penetrates the material up to several micrometres and eventually is scattered from atoms in different atomic layers or planes. The scattered x-ray beams then interfere with each other. Constructive interference is possible as the wavelength of X-rays and the distance between the atomic layers are of the same order \( \sim 10^{-10} \text{m} \). The interference being constructive is governed by Bragg’s law. Bragg’s law in real space is given by the following equation.

\[
2d \sin \theta = n\lambda
\]  

(1)

Where \( d \) is the spacing between the adjacent atomic planes, \( \theta \) is the scattering angle, \( n \) is an integer and \( \lambda \) is the wavelength of X-ray.

Bragg’s condition for constructive interference in reciprocal space is represented by the following equation

\[
\vec{G} = \Delta \vec{k} = \vec{k}' - \vec{k}
\]  

(2)

Where \( \vec{G} \) is the reciprocal lattice vector, \( \vec{k}' \) is the scattered wave vector and \( \vec{k} \) is the incident wave vector.
The diffraction pattern obtained is then compared with reference diffractograms from an internationally recognized database of literature reports.

There are many different types of methods to scan the sample. The method used in this work is the 0-2θ scan.

### 4.2.1 0-2θ Scan

Often 0-2θ diffractometer is used for measuring the position and intensities of Bragg reflections [39]. The schematic of this diffractometer is shown in fig.7. The diffractometer generally consist of an X-ray source, the slits to adjust the shape of beam, the sample and the detector. The spherical geometry ensures that the distance of X-ray source and detector remain constant from the sample. Since the analysis of surface layers is of the interest, the sphere reduces to a hemisphere. The name 0-2θ is based on the understanding that the variation of exit angle is determined with respect to the extended incoming beam and this angle is always 2θ for all points in the scan.

![Figure 7. Schematic representation of 0-2θ scan (after [39]).](image)
The Bragg condition in reciprocal lattice is fulfilled only if eq2 is met. i.e only those points contribute to the constructive interference which intersect the Ewald’s sphere. The theta-2theta scan probes the reciprocal space for constructive interference by varying the magnitude of reciprocal lattice vector $\vec{G}$ or $\Delta \vec{k}$, while keeping its orientation fixed to the sample normal as shown in fig.8. This results in the data of Intensity Vs. 2θ showing only those peaks at the detector for which the Bragg’s condition is fulfilled.

![Diagram](image)

**Figure 8. 0-20 scan in reciprocal space.**

### 4.3 Nanoindentation

Indentation techniques are generally used to measure the hardness of materials. Definition of hardness as the resistance to plastic deformation is at the core of each indentation technique and all techniques calculate hardness ($H$) as the ratio of the applied load ($P$) to area of the residual indent ($A$).

$$H = \frac{P}{A} \quad (3)$$

Experimentally it is achieved by pressing a hard tip with known mechanical properties, with a user defined load, into the material whose hardness is desired to measure. The residual indent
area ($A$) may then be calculated by for example optical means which then is substituted in eq.(3) along with the known load ($P$) to get the hardness ($H$).

In nanoindentation the load is in the milli-newton range that leaves the residual indent area of the order of few square micrometers or nanometers. This makes the optical method to measure residual area redundant. Thus instead of residual indent area, the area under the contact is used. To measure the area under the contact, the indentation depth and the known shape and the area of indenter are used.

There are many indenters available with different geometry. The indenter used in this work is the Berkovich indenter. This indenter has a pyramid shape and the contact area of an ideal Berkovich indenter is calculated by eq.(4).

$$A = 24.5h_c^2$$  \hspace{1cm} (4)

Where $h_c$ is the contact depth. The schematic cross-section through an indent left by Berkovich indenter is shown in fig.9.

Figure 9. Schematic of cross-section through an indent (after[40])
As shown in fig. 9.

\[ h_c = h_{\text{max}} - h_s \]  \hspace{1cm} (5)

Where \( h_{\text{max}} \) is the depth achieved at maximum load \( P_{\text{max}} \), \( h_s \) is the surface displacement.

Since during both loading and unloading the indentation depth is continuously recorded so \( h_{\text{max}} \) is known but \( h_s \) must be determined. The surface displacement can be written as

\[ h_s = \epsilon \frac{P_{\text{max}}}{S} \]  \hspace{1cm} (6)

Where \( \epsilon \) is a constant and depends upon the shape of the indenter. For Berkovich indenter it is equal to 0.75 [40]. \( S \) is the contact stiffness and is dependent on the material. It is the slope of load vs. displacement curve at maximum load as shown in fig.10. It is given by

\[ S = \frac{dP}{dh} \]  \hspace{1cm} (7)

![Figure 10. Load vs. Displacement curve](image)

As the tip of indenter can get blunt with usage thus a term having area function correction is added to eq.(4).
5. Experimental Details

Pre-depositon treatment of the substrates was performed by cleaning the WC-Co substrates in ultrasonic baths of alkali solution and alcohol.

The substrates were then mounted onto the rotating drum fixture of an industrial Sulzer/Metaplas MZR-323 reactive cathodic arc evaporation system equipped with compound cathodes in an atmosphere of nitrogen. Three circular cathodes, each with a diameter of 63mm, were mounted vertically in line with a separation of 15cm on one of the cathode flanges of the deposition chamber. The compositions of the cathodes were Zr$_{20}$Al$_{80}$, Cr$_{33}$Al$_{67}$, Cr$_{50}$Al$_{50}$ and Zr. The vertical placement as well as the difference in compositions of the cathodes results in a varying deposition flux over the height of the drum fixture providing a gradient in the compositions of the coatings depending upon the position of the substrates in the line of sight of the cathodes. The WC-Co substrates were equidistantly positioned in 5 rows along the height of the drum fixture with the cathode to substrate distance of about 15cm.

The system was then evacuated to a pressure of less than $2.0 \times 10^{-3}$ Pa. The substrates were then sputter sputtered with Ar ions. The deposition was then carried out with a cathode
current of 60A in 4.5Pa of N₂, a fixed substrate bias of -40V at about 500 °C while maintaining the drum rotation of 3rpm for two hours resulting in a coating of ~3µm.

Post deposition isothermal annealing was carried out at the starting temperatures of 800, 900, 1000 and 1100 °C for two hours in an argon environment at an atmospheric pressure using Sintervac furnace from GCA Vacuum Industries. The Samples were annealed with a rate of 7 °C/min till the temperature went down to 40 °C below the starting temperature. The rate was then reduced to 5°C/min. The samples were eventually cooled to 500 °C in 1.5 hours and further cooled to 100 °C in 4 hours.

Compositions of the coatings were established by EDX. This is done with Leo 1550 Gemini scanning electron microscope which was operated at 20kV, maximum magnification and a working distance of 8.5mm. The EDX was first calibrated with Cu reference sample. The yielded compositions in this work ranged from $\left(Zr_{x}Cr_{y}Al_{z}\right)_{1}N_{1}$ 0.01<x<0.81, 0.09<y<0.54 and 0.10<z<0.72 (x+y+z = 1).

XRD was performed with X’ Pert PRO from PANalytical using Cu-Kα radiation. The scan mode of 0-20 was selected with 20 ranging from 30° to 50°.

Hardness of the coatings was determined by nanoindentation. Nanoindentation was performed with CISRO UMIS nanoindenter fitted with Berkovich diamond indenter. Fused silica was used as a reference. The samples for nanoindentation were prepared by grinding and polishing the cross section of coatings mounted in Bakelite. The samples were then cleaned with acetone. An optimum load of 33mN was selected for which the penetration depth was around 0.20µm, which is within 10% of the coating thickness [41]. On each sample 40 indents were performed and then the average hardness was calculated
6. Results and Discussion

Based on the methods and techniques used, the results of thermal stability of ZrCrAlN material system are presented here.

6.1 Compositions

Out of an enormous sea of possible coating compositions, only 14 different compositions are deposited as shown in fig.11. The choice of these coatings is not random but rather systematic.

In ZrAlN the solubility of ZrN in AlN is very limited compared to all the investigated metal aluminium nitrides [33]. ZrAlN coatings can keep stable cubic structure up to the AlN concentration of 36% [34], beyond which the cubic AlN(c-AlN) transforms into hexagonal AlN (h-AlN) and the hardness decreases. CrAlN on the other hand has a highest solubility of CrN and AlN among all the investigated metal nitrides [42]. CrAlN coatings retain the cubic structure for AlN concentration of less than 77% [43].

Since ZrCrAlN has both ZrN and CrN the solubility limit of the whole system for the cubic structure is expected to have a value in the range of 36% -77% AlN concentrations. This is the reason why most of the deposited coatings lie between the range of 40% - 70% AlN concentration.
The deposited coatings can be broadly categorized with three different aluminium compositions, namely 40%, 50% and 70%.

![Figure 11. Deposited compositions of ZrCrAlN system](image)

**6.2 General Trends of As-Deposited Hardness vs. Zr Content**

The hardness trends of 40%, 50% and 70% groups of as-deposited coatings with respect to Zr concentration are shown in fig.12.
6.2.1 40%Al

As fig. 12 demonstrates, the 40% Al coatings show a steady increase in as-deposited hardness from 28 GPa to 33 GPa as Zr content is increased from 1% to 13%. The addition of c-ZrN in the matrix of c-ZrCrAlN creates a lattice mismatch which gives rise to coherency strains. These strains impede the motion of dislocations that explains the increase in hardness. The structure of these coatings remains cubic for the available Zr compositions. From the XRD graph in fig. 13 it can be seen that as the Zr content is increased both peaks (111) and (200) of the solid solution shift towards smaller angle indicating that the added Zr forms a solid solution with CrAlN which results in an increased lattice constant.
For this category, the as-deposited hardness curve displays an increasing trend all the way to the solubility of 13% Zr. The ascending hardness curve suggests that the cubic structure will be stable beyond 13% Zr until the solubility limit of Zr is reached. In light of this, it can be explained that coatings with comparatively low Al content (40%) can accommodate considerably high Zr content (≥ 13%) while keeping the cubic structure intact.

Figure 13. XRD Graph of 40%Al category
6.2.2 50%Al

For 50% Al, the as-deposited hardness rises from 29GPa to 34GPa as the Zr content is increased from 2% to 15%. The reason for the increase in hardness is same as that for the 40% Al category. The accompanying XRD graph is shown in fig.14. The structure remains cubic for the compositions at hand of this category of coatings. Just like 40% Al category the solid solution’s peaks (111) and (200) shift towards the left again indicating an increase in lattice parameter due to addition of Zr atoms.

![XRD Graph of 50%Al category](image)

Figure 14 XRD Graph of 50%Al category
6.2.3 70% Al

The 70% Al coatings exhibit a sharp decrease in hardness from 33GPa to 22GPa as the concentration of Zr is increased from 1% to 17%. With increase in the concentration of Zr the solid solution peaks (111) and (200) disappear in the XRD plots in fig.15 suggesting that the structure becomes amorphous which explains the decreasing hardness trend shown in fig 12 of this category. Like the aforementioned categories the shift in solid solution peaks with addition in Zr from 1% to 8% is due to the increase in lattice parameter.

![Figure 15 XRD Graph of 70% Al category](image)
Compared to 40% and 50% categories the solid solution peaks for the lowest Zr content is more towards AlN, which justifies a higher Al content. In all the above mentioned categories the XRD graphs show ZrO$_2$ peak at an angle of 34.8°.

6.3 Thermal Stability

Thermal stability of ZrCrAlN system is discussed in comparison with ZrAlN and CrAlN systems.

6.3.1 ZrAlN

The hardness values of two samples belonging to 70% Al category annealed at different temperatures are plotted with the documented Zr$_{0.44}$Al$_{0.56}$N coating [2] in fig.16. The post deposition annealing of Zr$_{0.44}$Al$_{0.56}$N is shown to result in significant age hardening with a hardness increase of 36%[2]. Zr$_{0.17}$Cr$_{0.16}$Al$_{0.67}$N and Zr$_{0.16}$Cr$_{0.12}$Al$_{0.72}$N demonstrate similar trends of age hardening. The age hardening in the case of Zr$_{0.16}$Cr$_{0.12}$Al$_{0.72}$N is found to be 33% which is a significant increase in hardness among the multinary coatings.
Figure 16. Hardness vs. Annealing temperature of ZrAlN[2] and ZrCrAlN

The XRD plots of both Zr$_{0.17}$Cr$_{0.16}$Al$_{0.67}$N and Zr$_{0.16}$Cr$_{0.12}$Al$_{0.72}$N given in fig.17 and fig.18, show the crystallization from the amorphous phase. The preferred orientation of crystallization is (111) and (200) with the precipitation of hexagonal AlN.

In the case of Zr$_{0.44}$Al$_{0.56}$N [2], it was reported that the amorphous phase comprises of hexagonal and cubic domains. During annealing the cubic domains grow while hexagonal domains remain small; however, at the annealing temperature of 1200°C the hexagonal domains grow big leading to the decrease in hardness.

In the case of Zr$_{0.17}$Cr$_{0.16}$Al$_{0.67}$N and Zr$_{0.16}$Cr$_{0.12}$Al$_{0.72}$N, the increase in hardness even in the presence of h-AlN at 1100°C can be explained by the observation for the CrAlN [44] system. The observation is that the precipitates of h-AlN hinders the plastic deformation as long as the h-AlN phase is small in size, evenly distributed and only a small volume fraction [44].
Figure 17. XRD graph of $\text{Zr}_{0.17}\text{Cr}_{0.16}\text{Al}_{0.67}\text{N}$
The XRD graphs in fig 17 and 18 show ZrO₂ peak at 34.8°. As this oxide peak apparently has no detrimental effect on the hardness values thus it can be regarded as a surface oxide layer.

To conclude, the addition of Cr has no detrimental effect on the pronounced age hardening which is the unique feature of ZrAlN[2] in ternary nitride coatings. The hybrid coating ZrCrAlN thus offer significant age hardening in multinary nitrid coatings.

6.3.2 CrAlN

Hardness of Cr₀.₄₄Al₀.₅₆N [44] and Zr₀.₀₇Cr₀.₄₀Al₀.₅₂N annealed at different temperatures is plotted in fig.19. In the case of Cr₀.₄₄Al₀.₅₆N [44] it was reported that the hardness stays at
around 29GPa till the temperature of 900°C is reached. Precipitation of h-AlN was then reported with further annealing and the sharp decrease in hardness was observed. For Zr$_{0.07}$Cr$_{0.40}$Al$_{0.52}$N the hardness value stays around 32GPa to the annealing temperatures up till 900°C. The precipitation of h-AlN at 1000°C is visible in XRD graphs shown in fig.20. This decrease in hardness at 1000°C is due to the fact that after the precipitation of h-AlN the lattice mismatch becomes very high. Consequently, the material becomes soft.

Figure 19. Hardness vs. Annealing temperature of CrAlN[44] and ZrCrAlN
With this comparison it can be summarized that the introduction of 7% Zr in Cr$_{0.44}$Al$_{0.56}$N does not deteriorate its stable hardness behaviour for the temperature range of 400°C – 900°C. The material system thus formed Zr$_{0.07}$Cr$_{0.40}$Al$_{0.52}$N which exhibits the similar stable hardness behaviour for the same range of temperature with higher hardness.

In CrAlN coatings one of the biggest factors for the decrease in hardness is the precipitation of h-AlN[3]. In present work it is seen that the precipitation of h-AlN is delayed by the addition of Zr. One such example is Zr$_{0.08}$Cr$_{0.28}$Al$_{0.64}$N. The reported precipitation of h-AlN in Cr$_{0.32}$Al$_{0.68}$ [44] is at 750°C. However in this research, it is observed that for
Zr$_{0.08}$Cr$_{0.28}$Al$_{0.64}$N the precipitation starts at 900°C this can be viewed in XRD graph shown in fig. 21.

Figure 21. XRD plot of Zr$_{0.08}$Cr$_{0.28}$Al$_{0.64}$N

The hardness of Cr$_{0.32}$Al$_{0.68}$ was reported to fall sharply above the annealing temperature of 900°C, whereas the hardness of Zr$_{0.08}$Cr$_{0.28}$Al$_{0.64}$N stays around 30GPa even at the temperature of 1100°C. The hardness vs. annealing temperature of Zr$_{0.08}$Cr$_{0.28}$Al$_{0.64}$N and Cr$_{0.32}$Al$_{0.68}$N is plotted in fig 22.
This leads to the conclusion that the addition of Zr in the ternary CrAlN not only retains the stable hardness behaviour but also provides thermal stability to the system by delaying the formation of h-AlN.

### 6.4 Structural Information

The general structural information gathered from this work about the ZrCrAlN material system is shown in fig 23. The structure is generally cubic but is amorphous for Al ≥ 67%, Cr ≥ 16% and Zr ≥ 17%.
Figure 23. Structural information of ZrCrAlN
7. Conclusion

Significant age hardening and delayed formation of h-AlN proved that ZrCrAlN has shown good thermal stability. This warrants the need to explore this system further.
8. Future Outlook

Thermal stability shown by ZrCrAlN provides the motivation to explore this system further.

Magnetron sputtering system will give a precise control over the coatings compositions which will be beneficial for the further exploration.

Transmission Electron microscopy and X-ray photoelectron spectroscopy can augment the results from structural character characterization in this thesis work.

Studies in Multilayers of different material systems have proved better thermal stability. Multilayers of this material system with other systems will be an interesting study.
9. References


