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# Predicting high temperature mechanical properties of CrN and CrAlN coatings from *in-situ* synchrotron radiation X-ray diffraction

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ABSTRACT

This contribution investigates the phase composition of CrN and CrAlN coatings by *in-situ* high temperature synchrotron radiation (SR-XRD), with the coatings deposited on steel substrate by closed field unbalance magnetron sputtering. Rietveld refinement on the SR-XRD spectra indicated CrN as the major phase, over the temperature range of 25 °C – 700 °C, for both coatings. At the high temperature of 700 °C, a $Cr_2N$ phase was observed in the CrN coating while the CrAlN coating also had a Cr phase. Williamson–Hall plots, from the refined data, afforded estimating variations of the strain and crystallite size of the major phase, up to 700 °C. The crystallite size (10 nm) for the CrAlN coating, at 25 °C, agrees very well with previous GI-XRD and TEM results obtained at room temperature Li et al. (2012).

## 1. Introduction

Magnetron-sputtered hard-surface coatings composed of transition metal nitride have been utilised to improve the productivity of cutting machinery in a wide range of applications such as drills, mills and cutting tools [2–4]. The main merit of magnetron sputtering is the attainment of robust control of the composition and microstructure of hard films and other nanostructured composite materials [5].

Due to their exceptionally high hardness characteristics and outstanding wear resistance, TiN coatings are major component in cutting machinery. However, TiN coatings exhibit only moderate resistance to oxidation and corrosion lessening their duration of use. In contrast CrN coatings display enhanced performance under oxidative and corrosive conditions that is primarily derived from the formation of an isolating adhesive chromium oxide layer on the coated surface [6]. In some applications, the thickness of film coating is an important parameter in deciding the type of coating to use. The maximum thickness of TiN coatings is typically limited to 10 μm, while CrN coatings can be made with thicknesses of more than 40 μm [7]. However, CrN coatings are associated with significantly lower hardness (*i.e.* 12.0–18.0 GPa), compared with TiN coatings (>20 GPa). The demand for improved properties has resulted in development of ternary and multinary coatings such as CrAlN, CrAlYN, CrSiN, CrAlSiN and CrAlTiN [8].

Incorporating (alloying) Al in the cubic lattice of c-CrN coatings forms a metastable phase that considerably improves the hardness of the coating. Since c-CrN exhibits high solubility for c-AlN, ternary CrAlN nanocomposite coatings are promising pseudo binary nitrides in which Al and Cr sesquioxides provide effective resistance against oxygen diffusion through the coating [9]. Outward diffusion of Cr and Al ions, to the surface in CrAlN coatings, results in the formation of complex surface oxides which enhance the thermal properties of CrAlN by acting as barriers against further oxidation [5]. Additionally the hardness and thermal stability of CrAlN are enhanced by Al substitution of Cr atoms in the face-centred cubic structure of c-CrN [8]. The solute atoms are believed to hinder slip by diffusing to and segregating around dislocations [10]. These two hardness-enhancing mechanisms in coatings are determined by the Al content and are characterised by formation of a metastable solid solution that produces internal lattice strains. Properties of such coating are highly sensitive to Al content where excessive addition of Al beyond 64 at.% alters the structure from rock-salt (NaCl) crystal structure (Fm3m) to wurtzite structure (P-31 m) resulting in deterioration of hardness and anti-oxidation

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properties with alteration of preferred growth orientation [11]. Formation of hexagonal h-AlN structures significantly decreases hardness and thermal stability of CrN coatings reducing the benefit of Al alloying [12].

High temperature properties of hard coatings primarily depend on their crystalline-phase structures. Alloying elements, present in the phase formed during the deposition stage, exert a noticeable influence on the durability and the expected service life of hard coatings [13–19]. Any significant variations in grain size of coatings may affect their thermal stability [20]. Therefore, any unforeseen changes in microstructure and phase composition of coating material can potentially reduce the thermal resistance and hardness [21] of the coatings. Since coatings deposited by the sputtering techniques are in a non-equilibrium condition [22], it is of vital importance to study the microstructure of the coatings at elevated temperatures.

Literature articles and reviews discuss overall mechanical and thermal properties including various preparation techniques of CrAlN coatings, in terms of their microstructure [23], effects of atomic ratio (*i.e.* Al/Cr ratios) on their phase composition [2,24], deposition control parameters [25,26], and high temperature oxidation properties [18,19].

Tribological properties of CrN coatings with Al and Si dopants deposited by cathodic arc, studied by Polcar *et al.* [27], showed high hardness, excellent oxidation resistance and thermal stability up to 800 °C. X-ray analysis showed that, the dominant structure in Al and Si-doped coating material was cubic solid solution of Al in CrN. However, hexagonal AlN was also detected in the AlCrSiN coating. Sánchez-López *et al.* [12] studied the tribological behaviour of CrAl(Y,Zr)N coatings at 300, 500 and 650 °C, and concluded that the CrAlN coating had lower film wear due to high hardness and presence of $Al_2O_3$ on the coating surface. Forsen *et al.* [28] reported improved hardness of CrAlN coating by addition of Ti which improves the formation of h-AlN at annealing temperatures up to 1100 °C. The enhanced hardness was due to spinodal decomposition into coherent TiCr and Al-rich structures of the coating material, causing age hardening that stabilised the significantly improved hardness. Wang *et al.* [18] deposited CrN and CrAlN using single electron beam plasma assisted physical vapour deposition (PAPVD) system, annealed them at 500 °C–1000 °C and then cooled down to 25 °C for characterisation. Their analysis showed orthorhombic CrN structure in the CrN coating, CrN was converted to β-$Cr_2N$ at about 500 °C and $Cr_2O_3$ was detected above 700 °C. A solid solution of (Cr,Al)N was detected in the CrAlN coating and was stable up to 900 °C. The hardness of CrN coating dropped from 24.8 GPa to 16 GPa at 600 °C. On the other hand, the original hardness of CrAlN amounted to 30 GPa which decreased to 21.6 GPa after annealing at 600 °C. CrAlN solid solutions can be deposited with up to 66.0 at.% of Al input [29,15], which precipitates into a more stable h-AlN phase with low mechanical properties, above 800 °C, as a result of a spinodal reaction [30].

Kirchlechner *et al.* [31] studied the deposition of CrN coating by reactive magnetron sputtering at temperatures of 25 °C – 850 °C. They employed high intensity synchrotron radiation beamline to obtain diffraction spectra from both coating and steel substrate simultaneously which enabled determination of strains and internal stresses of the coating and the substrate. Rivadulla *et al.* [32] used synchrotron radiation ($\lambda = 0.44397$ Å) in combination with *ab initio* calculations to identify the cubic to orthorhombic transformation of CrN at pressures of about 1 GPa. This transformation reduces the bulk modulus of the coatings.

The promising properties of CrAlN coatings highly depend on their complex phase behaviour and more detailed studies on their nanostructure could lead to fabrication of improved hard coatings. In our previous studies [2] [1], we employed multiple surface and subsurface analysis characterisation techniques to investigate $Cr_xAl_{1-x}N$ coatings on various substrates. Results revealed the formation of CrAlN solid solution, with amorphous AlN present at columnar CrN grain boundaries. The next step necessitates an accurate investigation of the role of Al on the change of crystal structure phases of CrN coatings at temperatures up to 700 °C. We explore the phase composition and crystal structure of the aforementioned coating in the temperature range of 25 °C to 700 °C using *in-situ* SR-XRD measurements. Finally, we analysed the SR-XRD measurements to derive the crystallite size and strain of the main phases up to 700 °C.

### 1.1. Experimental procedure

CrN and CrAlN coatings were deposited on M2 high speed steel substrates using closed field unbalanced magnetron sputtering system (Teer Coatings Ltd., UK) with four-target configuration. The coating process has been described in detail elsewhere [1,33]. To observe a phase formation in the CrAlN coatings, *in-situ* SR-XRD measurements were carried out as a function of temperature. Synchrotron radiation has a number of advantages including the ability to tune the wavelength to avoid the formation of sample fluorescence, superior energy bandpass and significantly higher signal/noise (S/N) compared to a laboratory instrument. The experiment was performed on the Powder Diffraction beamline at the Australian Synchrotron with monochromated X-rays of wavelength 0.82647 Å. The X-ray diffraction data were collected on a Mythen microstrip detector and the wavelength was determined by Rietveld refinement of a Standard Reference Material, LaB6 660b, as supplied by the National Institute of Standards and Technology (USA). The coated substrates were mounted on a Pt heating strip in an Anton Paar HTK-2000 high temperature furnace and aligned to the centre of rotation on the diffractometer. The samples were heated from ambient temperature up to 700 °C with a heating rate of 10 °C/min and X-ray diffraction data were collected over the angular range $10° \leq 2\theta \leq 89°$. The sample surface temperature was calibrated before experiment.

Samples made with CrN coating on M2 steel will be denoted as CrN-M2ST and samples made with $Cr_xAl_{1-x}N$ coating on M2 steel will be denoted as CrAlN-M2ST.

### 1.2. Theoretical procedure

In the present study, assuming Bragg–Brentano geometry, phase analysis of SR-XRD data was performed by the Rietveld method using the GSASII software package [34]. Initially refinement was applied to the unit cell parameter while all other structural parameters were fixed to the original standard values of the JCPDF data files listed in the results and discussion section. The crystal strain, atomic position, atomic isotropic temperature, zero shift, background as Chebyshev polynomial of fifth degree, peak profile, sample displacement and texture were then successively refined. The fittings were performed using analytic Hessian refinement derivatives. These corrections help to obtain physically realistic intensities, displacement and peak width models when analysing diffraction patterns in non-standard geometries.

## 2. Results and discussions

The coating composition was analysed at room temperature by X-ray Photoelectron Spectroscopy (XPS) [1] and the results are listed in Table 1.

The phases found in the coatings, from SR-XRD, are: CrN (JCPDF 011-0065), AlN (JCPDS 046-1200), Al (JCPDS 004-0787), $Cr_2N$ (JCPDS 00-035-0803), Cr (JCPDS 00-900-8467) and $AlO_2$ (JCPDS 00-901-1413) on a substrate of Fe (JCPDS 006-0696) dominated M2 steel. For clarity, only the Miller indices of appropriate phases are indicated in the SR-

**Table 1**
Contents of coating sample obtained from XPS measurements.

| | Concentration at. % | | | |
|---|---|---|---|---|
| Samples | Cr | Al | N | O |
| CrAlN-M2ST | 27.5 | 14.2 | 31.8 | 26.6 |
| CrN-M2ST | 49.6 | – | 30.3 | 20.1 |