Investigation of the Nanostructure and Wear Properties of PVD CrCuN Nanocomposite Coatings

M.A.Baker¹, P.J.Kench¹, C.Tsotsos², P.N.Gibson³, A.Leyland², A.Matthews²

¹School of Engineering, University of Surrey, Guildford, Surrey, GU2 7XH, UK

²Department of Engineering Materials, University of Sheffield, Portobello Street,
Sheffield, S1 3JD, UK

³Institute for Health and Consumer Protection, Joint Research Centre, I-21020 Ispra (VA)
- Italy

Abstract

This paper presents results on the PVD CrCuN nanocomposite coating system, in which the immiscibility of Cr (containing a supersaturation of nitrogen) and Cu offers the potential of a predominantly metallic (and therefore tough) nanocomposite, composed of small Cr(N) metallic and/or β -Cr₂N ceramic grains interdispersed in a (minority) Cu matrix. A range of CrCuN compositions have been deposited using a hot-filament enhanced unbalanced magnetron sputtering system. The stoichiometry and nanostructure have been studied by XPS, TEM, SEM and XRD. Hardness, wear resistance and impact resistance have been determined by nanoindentation, reciprocating-sliding and ball-on-plate high-frequency impact. Evolution of the nanostructure as a function of composition and correlations of the nanostructure and mechanical properties of the CrCuN coatings are discussed. A nanostructure comprising of 1-3 nm α -Cr(N) and β -Cr₂N grains separated by intergranular regions of Cu give rise to a coating with significantly enhanced resistance to impact wear.

Keywords: CrCuN, nanocomposite coatings, nanostructure, wear, PVD

1. Introduction

It is well known that tailoring the nanostructure of coatings offers the potential of enhanced mechanical properties. The nanocomposite architecture of embedding hard nanocrystallites in an amorphous matrix, has become accepted as a design concept to increase the hardness, toughness and wear resistance of coatings for machine parts and tools [1-3]. Most ceramic materials used as protective coatings exhibit high hardness and elastic modulus. There is evidence to suggest that a high elastic modulus is often not ideal for improving the impact and sliding wear resistance of metallic components. For certain manufacturing operations (e.g. punching and forming), extending the lifetime of the machine tool requires a coating which has a strong resistance to fretting and the ability to deform without undergoing brittle or adhesive failure. Thus, for metallic substrates, desirable coating material properties are a combination of relatively high hardness and relatively low modulus: the latter being closely matched to that of the substrate [4].

It is within this context that metallic CrCuN coatings are being deposited. Rebholz et al have shown that adding up to 16 at.% N to Cr yields coatings in which N is interstitially incorporated in α -Cr [5]. Increasing the N content to between 16 and 29 at.% gave rise to a dual phase α -Cr(N) + β -Cr₂N structure. Both single phase Cr(N) and dual phase Cr(N) + Cr₂N coatings offer good impact resistance, the former also exhibiting little evidence of radial cracking around the impact crater. By adding Cu to Cr(N), the aim is to deposit coatings having a structure of Cr(N) nanocrystallites interdispersed within a minority Cu matrix. There is a thermodynamic driving force for immiscible phases in a coating system to separate. In the Cr-Cu system, Cr prefers to adopt a b.c.c. and Cu a f.c.c. structure.

The equilibrium phase diagram shows only a very small solubility of Cr in Cu [6]. However, it was reported previously that metastable Cr-Cu single phase structures can be formed over a wide composition range using PVD methods [7-9]. Previous work on CrCuN coatings deposited at a substrate temperature of approximately 200°C, in which the Cu concentration was varied from 2 to 20 at.%, showed no clear evidence of Cu phase formation [10]. In this paper, the deposition temperature is increased to 300-350°C and Cu concentrations increased to over 55 at.%. The nanostructure of these coatings is examined using TEM, XRD and XPS with mechanical properties evaluated from reciprocating-sliding, impact and abrasive wear tests.

2. Experimental

CrCuN coatings were deposited by reactive unbalanced magnetron co-sputtering of Cr and Cu onto Si wafer, AISI 316 stainless-steel and M2 tool-steel substrates. The samples were sequentially pre-cleaned ultrasonically in acetone, isopropyl alcohol and methylated spirits (5 minutes each) and furnace dried at 120°C for 30 min. The samples were radiantly heated to approximately 300°C with the aid of a 2kW resistive heater, prior to sputter cleaning for 20 min. at 5 Pa argon pressure, with the substrate bias at -700 V and $\sim 0.5 \text{ mA/cm}^2$ substrate current density. The coating process was carried out at 3.5 mTorr Ar pressure with a 10 sccm N₂ flow rate. Two 380 mm x 100 mm x 6.5 mm rectangular sputter targets (one Cr and one Cu) were used, powered respectively at 1.5 kW and 0.15 kW; the substrate bias was set at -100 V with $\sim 0.3 \text{ mA/cm}^2$ substrate current density. The coatings were deposited at a substrate temperature of 300°C, rising to 350°C by the end of the deposition period. The Cr and Cu sputter targets were positioned on adjacent walls of the reaction chamber. To adjust the Cr/Cu ratio of the alloys, the specimens were placed towards the centre of the deposition chamber at varying intervals facing the

Cr and Cu targets which were each positioned at an angle of 45 degrees to the substrate holder. The specimens were placed such that coating 1 was nearest to the Cr target and coating 6 nearest to the Cu target.

X-ray Photoelectron Spectroscopy (XPS) was performed on a VG Scientific Sigma Probe employing a non-monochromated Mg-K α source and a spherical sector analyser. A 3 keV Ar⁺ ion beam was used to remove the surface oxide layer. Survey spectra of the bulk coating were then recorded at 50 eV pass energy and narrow scans at 20 eV pass energy (step width of 0.1 eV). Quantification was performed after a Shirley background subtraction using instrument modified Scofield sensitivity factors. XRD was performed using a Philips X-ray diffractometer, employing monochromated Cu-K α radiation at a tube voltage of 40 keV and current of 24 mA. A LaB₆ Philips CM200 operated at 200 keV was employed for the TEM work. Preparation of the cross-sectional TEM specimens involved using a Gatan Precision Ion Polishing System (PIPS) ion beam thinner with the beam incident first at 15 degrees, before a final thinning at 4 degrees. Two guns were used, one above and one below the specimen, each operating at an accelerating voltage of 5 keV and current of 1 mA. Plan view specimens were prepared by thinning through the substrate, leaving the surface of the coating sufficiently thin for investigation.

For coatings deposited on AISI 316 substrates, the wear resistance properties were determined as follows. Reciprocating-sliding wear was measured using a low frequency (5 Hz) reciprocating test apparatus, with a 10 mm diameter SAE 52100 ball counterface, at 10 N normal load, for 500 m sliding distance at a temperature of 23 $\pm$ 2°C and 50 $\pm$ 5% humidity. The average wear-scar cross-sectional area was measured using a Dektak 3ST surface profilometer and the wear rate calculated. To determine impact wear resistance, a

dynamic ball-on-plate impact tester, using a 10 mm diameter WC-6Co ball, impact force 1000 N, frequency 8Hz, was employed. Three samples of each coating were tested for 10^5 impact cycles. The impact crater diameter was measured for each and the average impact volume calculated.

3. Results

3.1. Composition (XPS)

Six CrCuN coatings with increasing Cu content were examined. The relative compositions and binding energies of the Cr 2p_{3/2}, Cu 2p_{3/2} and N 1s peaks determined by XPS are given in Table 1. The Cu concentration increased from 1.8 at.% for coating 1 to 55.5 at.% for coating 6. The N concentration remained moderately constant, varying from 18 to 23 at.% (except for coating 6, where the high Cu content led to a reduction in the N concentration to 14 at.%). The Cr/N ratios are also given in Table 1. In this ternary system, rather than using nitrogen concentration alone, the Cr/N ratio is a more useful gauge of the critical level of N supersaturation in Cr required to precipitate β -Cr₂N.

3.2. Diffraction (XRD and TEM)

The XRD patterns are presented in Figure 1. Coating 1 has the highest Cr concentration and the XRD pattern is dominated by the single α -Cr (110) peak. Consequently, the 18 at.% N appears to be mainly incorporated interstitially in the α -Cr phase. There is a pronounced Cr (110) peak shift to higher angles, indicative of a slightly reduced lattice parameter, probably due both to the incorporation of N in the crystallites and in-plane stresses as a result of the deposition process. Coating 2 shows the clear emergence of the β -Cr₂N (200) peak in addition to the Cr (110) peak and similar patterns with both peaks

present are seen for coatings 3 and 4. (In a randomly oriented material, the β -Cr₂N peak would be very weak, but Cr₂N coatings with a strong (200) orientation can result from reactive magnetron sputtering [11]). A slight decrease in the Cr/N ratio (and total supersaturation of (Cu + N) in Cr) has resulted in the precipitation of the Cr₂N phase in addition to Cr(N). From coating 2 to coating 4 there is a progressive increase in the Cr₂N/Cr peak intensity ratio and an incremental shift of the Cr (110) peak to lower angles. This progressive shift of the Cr (110) peak back towards its elemental position can be explained by a reduction of the N concentration in the Cr(N) supersaturated phase as the Cr₂N phase fraction increases, together with a modification of the in-plane stress.

A dramatic change in spectral peak shape is observed for coatings 5 and 6. For coating 5, the XRD pattern exhibits one broad peak characteristic of an X-ray amorphous structure, the maximum occurring at approximately 46.1° (d spacing = 1.97 Å). This maximum does not coincide with reflections for Cr, β -Cr₂N or Cu. However, as seen in Figure 2, electron diffraction results indicate the Cr-containing phases in this coating to in fact be nanocrystalline. The nanocrystallites of Cr and β -Cr₂N are very small and uniform in dimension, being approximately 2 nm in diameter (see Figure 3). Consequently, for coating 5, XRD appears unable to yield structural information about the Cr-containing phases, but does provide evidence for an intergranular Cu amorphous phase (see below). The spectrum of coating 6 is comprised of three overlapping peaks. The main peak at 50° is indicative of nanocrystalline Cu phase formation. The intermediate peak has a maximum similar to that for coating 5 (at 46.1°) and the peak at low angles probably corresponds to the Cu (111) and/or β -Cr₂N (200) reflection. Thus, as the Cu concentration rises to 55 at.%, nanocrystallites are able to form and a three-phase Cu / Cr(N) / Cr₂N nanocrystalline structure emerges.

Electron diffraction patterns for the coatings are shown in Figure 2. Coatings 1-4 show a good correlation with the XRD spectra. Only one phase, α -Cr, was observed in coating 1 and two phases, α -Cr + β -Cr₂N, were clearly present in coatings 2-4. Faint and diffuse reflections were indexed to both Cr and Cr₂N phases for coating 5 (see section 3.4). In coating 6, in addition to the Cr and Cr₂N phases, some faint spots corresponding to the Cu (200) reflection are discernable.

3.3. Bonding (XPS)

Regarding chemical state and bonding information, there was no significant variation in the XPS core level peak positions and shapes between the coatings (Table 1). The Cr 2p_{3/2} peak position remained essentially unchanged at 574.4 ± 0.1 eV. The value is similar to that obtained for pure Cr (574.5 eV – as measured separately on our spectrometer) and Cr₂N (574.8 eV [11]). Little variation is also observed for the N 1s peak position. The N 1s energies (397.5 ± 0.1 eV) are similar to the literature values for Cr₂N [12]. Nitrogen atoms will be present both as nitrides and at interstitial locations within the Cr phase. The Cu 2p_{3/2} peak shows a trend of decreasing binding energy with an increase in the Cu concentration (although the shift is very small). The binding energy progressively changes from 933.0 eV to 932.7 eV as the Cu concentration is increased. A similar variation of 933.1 eV for low Cu concentration samples increasing to 932.8 eV for high Cu concentrations was also observed in our previous work on CrCuN [10]. For coating 6, the Cu concentration reaches 56 at. % and from the XRD results, Cu can be identified as a separate phase. Consequently, it can be understood that the Cu peak tends to a binding energy of that for elemental Cu (i.e. 932.7 eV [13]) as clustering and eventual phase formation occurs with increasing Cu concentration.

3.4. Nanostructure (TEM)

Bright field (BF) and dark field (DF) plan view TEM images for coatings 1-6 are given in Figure 2. It should be noted that the BF and DF images are not necessarily from identical regions. DF images were formed from the α -Cr (110) and β -Cr₂N (200) reflections. All coatings are nanocrystalline, although there are substantial differences in the grain size and distribution between the various nanostructured phases present.

Coating 1 has a single phase metastable Cr(N) structure and a fairly uniform fine grain size. Coatings 2 and 3 exhibit a dual phase Cr(N) + Cr₂N structure and a larger distribution of grain sizes. (A cross-sectional TEM DF image of coating 3 is also given in Figure 3 (a). The structure in this image is consistent with the DF plan view image and also shows evidence of columnar growth.) The larger grain size for coatings 2 and 3 is apparently caused by nucleation of β -Cr₂N. Two possible effects can account for this: (a) the Cr₂N nanocrystallites once nucleated are able to grow from the surrounding α -Cr(N) matrix and/or (b) the previously high concentration of N at the grain boundaries in Cr(N), which would be expected to hinder grain growth, is reduced on nucleation of Cr₂N, facilitating grain coarsening. Coating 4 has a two phase Cr(N) + Cr₂N structure but exhibits a finer grain size than coatings 2 and 3. Compared to the latter two coatings coating 4 has a higher Cu concentration (approximately 8 at. %). In this case, the smaller grain size may be attributable to Cu segregating to grain boundaries and suppressing grain coarsening mechanisms.

The nanostructure of coating 5 is of particular interest. Consequently, in addition to the general plan-view images in Figure 2, a cross-section DF image, a second DF plan view

image and a higher resolution plan view DF image are also given in Figures 3 (b), (c) and (d) respectively. The nanocrystallite phase composition cannot be unambiguously determined from the electron diffraction pattern, it is either purely Cr(N) or a mixture of Cr(N) + Cr₂N. However, the low Cr/N ratio and high level of total supersaturation of N and Cu in Cr(N) most probably results in the formation of both phases. The nanostructure of this coating is very fine and uniform, with a consistent nanocrystallite size of 2-3 nm. There is strong preferential orientation of the nanocrystallites and columnar growth is evident from the DF cross-section image.

Even at 23 at. %, Cu has not formed as a separate nanocrystalline phase in coating 5. In view of the low solid state miscibility of Cu with Cr, the fine nanostructure and moderate deposition temperature, the majority of the Cu atoms may be expected to be located at grain boundaries and the position of the XPS Cu 2p_{3/2} peak is in accordance with Cu cluster formation. Thus a two component nanocrystalline/amorphous system can be assumed, the nanocrystalline components being either purely Cr(N), or Cr(N) + β -Cr₂N and the amorphous component being Cu. The relative atomic proportions of the two components are 77:23 (Cr+N):Cu.

Coating 6 has a three-phase structure. Increasing the Cu concentration to above 55 at.% has led to its precipitation as a separate metallic phase. The Cr and N concentrations are now much lower, but as the Cr/N ratio (at 2.2) is still low, both metallic Cr(N) and ceramic Cr₂N phases form in addition to Cu.

3.5. Hardness & wear resistance

Nanoindentation data taken at a 20 mN load is shown in Figure 4. The hardness for coating 1 is 25 GPa, rising to a maximum of 32 GPa for coating 3. From coating 4 to coating 6, the increasing Cu content causes the hardness to drop. The elastic modulus follows a similar trend. The H/E values vary between 0.085 and 0.01.

The reciprocating-sliding and impact wear results are given in Figs. 5 and 6 respectively. In both tests, the best wear rates were observed for coatings 3-5. In reciprocating-sliding wear tests, mild polishing wear of the counterface ball rather than the coating was observed for positions 3 and 5. Coating 5 performed best in impact wear tests. The wear crater volume of $5 \times 10^{-3} \text{ mm}^3$ was at least 3 times lower than for the other CrCuN coatings and about 35 times less than that observed for a single phase Cr(N) coating (N content 16 at.%) [5]. The SEM micrographs for coatings 1-4 show greater delamination and radial cracking outside the crater than coatings 5 or 6. The marked difference in performance between coatings 2 and 3 is difficult to rationalise considering their similar compositions and nanostructures. Nevertheless, the significant improvement in performance of nanostructured CrCuN coatings over a single-phase Cr(N) equivalent remains evident.

In abrasive wear tests (Fig. 7), the behaviour of the coatings is quite different. Only positions 2-5 were tested. The coating thicknesses decreased from coating 2 to 5 and this is reflected in the abrasion resistance results. Taking into account the influence of thickness variation, there appears to be little difference in the abrasion resistance, but coating 5 exhibited a slightly poorer performance than the other coatings. All coatings

however exhibit substantially improved abrasion resistance over the uncoated AISI 316 steel substrate.

4. Discussion

4.1. Formation of Cr(N) and Cr_2N

This set of CrCuN coatings has shown a very interesting evolution of nanostructure as a function of composition. Coating 1 is a single phase $\alpha\text{-Cr(N)}$ coating with a grain size of approximately 3-5 nm. As $\beta\text{-Cr}_2\text{N}$ is precipitated in all other coatings, it would appear that approximately 18 at.% (or a Cr/N ratio of 4.3) corresponds to the saturation limit of N in Cr. This is in good agreement with the 16 at.% N saturation limit found by Rebholz et al [5], for ‘pure’ Cr(N) coatings sputter deposited under similar conditions.

Incorporation of $\beta\text{-Cr}_2\text{N}$ into the coating structure has resulted from the decreasing Cr/N ratio as the Cu content increases. However, as suggested by the formation of Cr_2N in coating 3 (also having a Cr/N ratio of 4.3), the limiting N concentration may also be influenced by the total supersaturation concentration of [N+Cu] in Cr, so avoiding $\beta\text{-Cr}_2\text{N}$ formation may require an even lower N concentration. The total supersaturation concentration will also be dependent on the degree of phase separation that has taken place. Taking purely the Cr/N ratio as a measure of N concentration and a Cr/N ratio of 4.3 as the limiting value, for coating 5, (Cu content 23 at. %) an overall N concentration < 12.4 at.% would be required to form metallic Cr(N) as the only nanocrystalline phase.

Phase separation in nanocomposite coatings is dependent on both thermodynamic and kinetic considerations. From a kinetic viewpoint, surface mobility is critical and for any selected nanocomposite system composed of two stable phases, separation of the two phases will be promoted by *increasing* the deposition temperature. However, in the

CrCuN system, the situation is complicated by the fact that the desired hard phase, Cr(N) is metastable. Metastable phase formation is promoted by *reducing* the deposition temperature. Consequently, to achieve the desired nanostructure requires a deposition temperature which enables both competing processes, metastable α -Cr(N) phase formation and amorphous *a*-Cu phase separation, to simultaneously occur. Thus, compared to other nanocomposite systems composed solely of stable phases e.g. *nc*-(Ti,Al)N/*a*-BN [1] or *nc*-TiN/*a*-Si₃N₄ [2], deposition of the metallic *nc*-Cr(N)/*a*-Cu system may be possible only in a relatively small deposition-parameter temperature window. The deposition temperature of 300-350°C, -100 V substrate bias and ~ 0.3 mA/cm² current density combination of parameters employed here appear capable of forming purely Cr(N) when the Cr/N ratio > 4.3 .

According to the Cu-Cr phase diagram [14], the solubility of Cu in Cr is ≤ 0.02 %. However, it has been shown that sputtering at low temperature ($\leq 200^\circ\text{C}$) enables the range of Cu-Cr mutual solubility to be extended, resulting in metastable phase formation over much of, or the whole, Cu-Cr composition range [7-9]. In our previous set of CrCuN coatings, sputter deposited at 200°C with Cu contents up to 20 at.%, elemental chromium and chromium nitride nanocrystalline phases were clearly identifiable in the XRD spectra but we concluded that Cu was probably incorporated in the Cr-based phases rather than a nanocomposite structure developing [10]. Although the formation of an amorphous Cu intergranular phase and the location of most Cu atoms at grain boundaries cannot be unequivocally proven from the results obtained here, the very small grain size and form of nanostructure observed for coating 5 would suggest that a deposition temperature of 300-350°C is sufficiently high to effectively achieve separation into discrete Cu- and Cr-based phases in this case.

4.2. Grain size effects

In the general nanocomposite design proposed by Veprék [2], to achieve the desired mechanical properties, complete monolayer coverage of nanocrystallites by the amorphous phase is required. As the grain size changes, so does the surface area/volume ratio. Consequently, the critical concentration, C_c , of amorphous phase necessary to provide monolayer coverage, needs to be calculated for any particular grain size. For an idealised *nc*-Cr/*a*-Cu system, calculations have been undertaken to determine the C_c of Cu required to provide monolayer coverage of Cr as a function of grain size. As TEM or XRD can provide estimates of the grain diameter, it is appropriate to base the calculations on this as an input parameter. Calculations have been undertaken assuming the Cu monolayer to have one of two 2D packing densities: simple square packing or hexagonal close packing and results given for each case. Random close packing, (also known as dense random packing) has a packing density higher than simple square packing but lower than hexagonal close packing. A number of amorphous metal systems tend to such a structure [15,16] and for the amorphous Cu layer considered here, random close packing is probably the most appropriate packing density. However, calculations of the surface area/volume ratio are not easily undertaken for random packing arrangements and are consequently not presented.

The surface area/volume ratio for any given grain diameter is independent of whether the grain shape is approximated to a cube or a sphere (although the total number of atoms is different). Consequently, if it is assumed that monolayer coverage corresponds to half the total surface area (due to grains sharing surfaces) then the amount of Cu required for

monolayer coverage of grain diameter d , can be calculated for simple square packing from the following expression:

$$\frac{\text{No. of Cu atoms for monolayer coverage}}{\text{No. of Cr atoms in a cubic grain}} = \frac{3d^2/(2r)^2}{pd^3/V} = \frac{3V}{4pdr^2}$$

where r is the atomic radius (being taken as 0.125 and 0.128 nm for Cr and Cu respectively [17]), p is the packing density (e.g. 68 % for body centred cubic Cr) and V is the atomic volume. A similar expression is obtained for hexagonal close packing:

$$\frac{\text{No. of Cu atoms for monolayer coverage}}{\text{No. of Cr atoms in a cubic grain}} =$$

$$\frac{3d^2/(2r \times \sqrt{(2r)^2 - r^2})}{pd^3/V} = \frac{\sqrt{3}V}{2pdr^2}$$

The results are given in Table 2. The required Cu at.% range for random close packing would be expected to lie within the simple square packing – hexagonal close packing range. These results should clearly be taken as approximations but give working estimates of the range of minimum theoretical concentrations required to form a complete 3D-interconnecting network of the monolayer, for a given nanograin size. Furthermore, as all nanocomposite systems will exhibit similar grain-volume/surface-area ratios as a function of grain size, the trend in concentrations of amorphous phase required for monolayer coverage with decreasing grain size, should be representative of all such systems.

For *nc*-TiN/*a*-Si₃N₄ thin films, Veprek et al have also considered the effect of crystallite size on Si₃N₄ surface coverage of TiN nanograins [18]. They concluded that the Si₃N₄ surface coverage can be determined by multiplying the XPS Si 2p intensity by the grain diameter *d*. Applying a similar rationale to this system, multiplication of the required Cu content for monolayer coverage by the grain size (values given in Table 2) should give a constant for differing grain sizes. As the grain size increases from 1 – 10 nm, the product is however not constant, but shows a monotonic increase with grain size, demonstrating an inconsistency between the two methods of dealing with the effect of grain size. Although the approach of Veprek et al does provide a scaling in the amorphous phase fraction as a function of grain size, their methodology appears oversimplified.

Nevertheless, Veprek et al suggest that for *nc*-TiN/*a*-Si₃N₄ nanocomposites [18], at grain diameters of 3-4 nm, 17-23 mol.% Si₃N₄ corresponds to monolayer coverage of the grain. This is in reasonably good agreement with our calculations for the idealised *nc*-Cr/*a*-Cu system, where a 2-3 nm grain size corresponds to an expected amorphous phase concentration of approximately 20 at.% Cu for monolayer coverage.

From the results of the calculations given in Table 2, ignoring any effect of N incorporation in Cr, and assuming that phase separation is complete and that all grain boundaries are equivalent, then coating 5, with a Cu content of 23.4 at. % and an average grain size of approximately 2-3 nm, would have a sufficiently high Cu concentration for grain boundary monolayer coverage of the Cr-containing nanocrystalline phases.

4.3. Coating Growth Mechanisms

From the cross-sectional TEM images in Fig. 3, the CrCuN coatings can be seen to exhibit columnar growth. The columns of both coatings 3 and 5 have an average diameter of approximately 50 nm (Figures 3 (a) and 3 (b)) and grow vertically from the substrate. For coating 5, the strong preferential orientation of the small and uniform sized Cr based nanocrystallites in Figures 2 (j) and 3 (c) provide an interesting insight into the columnar growth mode. In TEM, 3D information is projected to form a 2D image. Consequently, it is reasonable to assume that the large irregular features in Figs. 2 (j) and 3 (c) (composed of many hundreds of nanocrystallites) correspond to individual columns. As the columns grow vertically, they extend laterally to produce fractal-like forms, very similar to 2-D sub-monolayer cluster model simulations at the percolation threshold [19,20]. Thus, the deposition conditions are such that lateral growth of the columns is developing in a random or disordered fashion.

The results in Table 2 indicate that ~23 at.% Cu is sufficient for complete grain boundary monolayer coverage in a *nc*-Cr/*a*-Cu nanocomposite. However, for coating 5, distinct preferential orientation of the nanocrystallites is observed. The initiation of (essentially) new crystallites in the same orientation would be promoted by incomplete grain coverage rather than full monolayer coverage. Consequently, although 23 at.% Cu is theoretically sufficient for monolayer coverage, in practice, the highly dynamic and chaotic solidification processes in such multi-component systems will most probably lead to clustering of the Cu at the grain boundaries rather than uniform monolayer coverage [4,10,21].

Considering the conclusions drawn from our previous work on sputter deposited CrCuN coatings deposited at 200 °C [10], it seems likely that, even at the higher deposition

temperatures employed here, the idealised nanocomposite structure is not actually being formed during growth. Instead, it is reasonable to expect a small percentage of Cu atoms remaining within the Cr based grains and the distribution of Cu at the grain boundaries to not be completely homogeneous.

To summarise, the analytical results suggest that for coating 5 we are *approaching* a nanostructure corresponding to α -Cr(N) + β -Cr₂N nanocrystallites (grain size 2-3 nm) separated by a Cu-rich amorphous grain boundary layer. Much of the Cu is located at grain boundaries, but probably clustered rather than forming a uniform monolayer – hence, the ‘idealised’ nanocomposite structure [18] is not fully developed. This coating is largely metallic in nature.

4.5. Nanostructure / Mechanical-Property Correlations

The CrCuN coatings show a range of nanostructures across the composition range. The best performing coating in both reciprocating-sliding and impact wear tests was coating 5. In this coating, the nanocomposite structure of Cr(N) + Cr₂N nanocrystallites mostly interdispersed by an amorphous Cu intergranular layer offers a superior combination of mechanical properties to resist these wear processes. Hard nanocrystallites of interstitially-supersaturated metallic Cr(N) and ceramic β -Cr₂N will provide resistance to indentation. During impact wear, a metallic substrate will deform and the capability of the coating to behave in a similar manner is important in preventing delamination and cracking over many cycles. Consequently, although hardness is primary in the protection of the underlying material, fracture and delamination generally lead to premature coating failure. Thus, prolonged coating integrity and adhesion to the substrate are the most influential factors in extending the lifetime of the coating in impact wear applications.

The presence of Cu at the grain boundaries will enlarge the grain boundary region, promoting grain boundary sliding and allowing local plastic deformation to occur. This may explain the general absence of delamination and radial cracking in the impact wear test results for coating 5. Furthermore, the general prevalence of metallic rather than ceramic bonding within the coating will enhance fracture toughness and act to lower the elastic modulus, improving adhesion.

In abrasive wear tests, coating 5 showed a slightly inferior performance than the other three coatings with lower Cu concentrations. This is perhaps not surprising, since in such abrasion tests there is negligible deformation of the substrate, fracture is not a common cause of early coating failure and hardness is the foremost property in the prevention of wear for such applications. β -Cr₂N is a phase with a high hardness and the β -Cr₂N/Cr(N) ratio increases progressively from coatings 1 to 4. Coatings 2 and 3 show good abrasion resistance, but in coatings 4 and 5, the positive effect of β -Cr₂N is negated by the increasing Cu concentration, reducing the hardness and, particularly in the case of coating 5, the abrasion resistance.

The excellent performance of coating 5 in impact and reciprocating-sliding tests is very encouraging. However, results of the nanostructural investigation suggest that for this coating the 'idealised' nanocomposite structure has not fully developed. Furthermore, many parameters are yet to be optimised for such systems, e.g. grain size and intergranular layer thickness. Consequently, significant further improvement in mechanical performance can be expected when the optimum composition and structure are attained.

5. Conclusions

A range of CrCuN coatings, with a N concentration of approximately 20 at.% and Cu contents ranging from 2 to 56 at.%, have been deposited by hot-filament enhanced reactive co-sputtering at a deposition temperature of 300-350 °C. All coatings exhibit a nanocrystalline or nanocomposite structure. The nanostructure varies as a function of Cu content as follows:

- (a) *coating 1*: at Cu contents below 2 at.%, a single phase α -Cr(N) structure is formed
- (b) *coatings 2-4*: at Cu contents of 3-9 at.%, a two phase α -Cr(N) + β -Cr₂N nanocrystalline structure is formed with Cu probably present at grain boundaries and within the nanocrystallites
- (c) *coating 5*: at a Cu content of 23 at.%, a two phase Cr(N) + Cr₂N structure develops with a crystallite size of 2-3 nm. Much of the Cu is located at grain boundaries, but the idealised nanocomposite structure with complete grain coverage is not fully developed.
- (d) *coating 6*: at a Cu content of 56 at.%, a three-phase Cu / Cr (N) / Cr₂N nanocrystalline structure is obtained.

Calculations for an idealised *nc*-Cr/*a*-Cu nanocomposite structure show that, for a grain size of 2-3 nm, monolayer coverage of the Cr grains should be obtained at a Cu concentration of approximately 20 at. %. However, the nanostructure of coating 5 suggests that not all the Cu has segregated to the grain boundaries and/or uniform monolayer formation does not occur in practice - hence intergranular coverage by the *a*-Cu phase is probably incomplete.

In impact wear tests, coating 5, having a $nc\text{-}[\text{Cr}(\text{N}) + \text{Cr}_2\text{N}]/a\text{-Cu}$ structure, shows an improvement by at least a factor of 3 over the other CrCuN coatings and is more than 30 times better than single phase Cr(N) [6]. This coating structure also performed best in reciprocating-sliding tests, but did not show improved abrasion resistance. The enhanced impact and reciprocating wear performance of coating 5 is attributed to the relatively high hardness (18 GPa) combined with excellent fracture toughness and adhesion to the substrate. For the $nc\text{-}[\text{Cr}(\text{N}) + \text{Cr}_2\text{N}]/a\text{-Cu}$ structure, toughness and adhesion are enhanced by: (a) predominant metallic bonding (giving a high H/E ratio); (b) the nanocomposite structure improving fatigue resistance and facilitating some plastic deformation by grain boundary sliding; (c) the ductility of Cu.

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Table 1: Relative atomic percentages of Cr, Cu and N; and the positions of the major photoelectron peaks as determined by XPS for the six CuCr (N) coatings.

Sample	Atomic Percent				Stoichiometry	XPS Peak Position (eV)		
	Cr	Cu	N	Cr/N		Cr 2p _{3/2}	Cu 2p _{3/2}	N 1s
Coating 1	79.8	1.8	18.4	4.3	CrCu _{0.02} N _{0.24}	574.3	933.0	397.5
Coating 2	76.4	3.0	20.6	3.7	CrCu _{0.04} N _{0.27}	574.4	932.9	397.6
Coating 3	78.5	3.3	18.2	4.3	CrCu _{0.02} N _{0.19}	574.3	932.9	397.6
Coating 4	70.5	8.4	21.1	3.3	CrCu _{0.12} N _{0.30}	574.3	932.8	397.6
Coating 5	53.3	23.3	23.4	2.3	CrCu _{0.44} N _{0.44}	574.4	932.7	397.5
Coating 6	30.7	55.5	13.8	2.2	CrCu _{1.81} N _{0.45}	574.3	932.7	397.4

Table 2: The atomic concentration of Cu required to give monolayer coverage of Cr grains in a Cr/a-Cu nanocomposite coating. The range of Cu at.% required corresponds to different Cu monolayer packing densities (associated with simple cubic packing or the closer packed hcp/fcc arrangement).

Cr grain size (nm)					
	1	2	3	5	10
Cu at. % required	35.6-38.9	21.6-24.2	15.5-17.5	10.0-11.3	5.2-6.0
	~4	~8	~12	~20	~80
Cr grain width (No. of atoms)

Figure 1: XRD spectra of the CuCr(N) coatings

Figure 2 : Plan view bright field (left) and dark field (right) TEM micrographs of CuCr (N) coatings. The figure progresses numerically from coating 1 ((a) and (b)) to coating 6 ((k) and (l)).

Figure 3: TEM dark field images of the CuCr (N) coatings (a) cross-section coating 3; (b) cross-section coating 5; plan-view coating 5; (d) high resolution plan-view coating 5

Figure 4: Nanoindentation hardness and elastic modulus results for coatings 1-6 determined at a load of 20 mN

Figure 5: Knoop microhardness results for coatings 1-6 at loads between 25 and 100 g.

Figure 6: Reciprocating wear rates for coatings 1-6

Figure 7: Impact wear results for the CuCr (N) coatings. WC-4Co ball counterface, 100,000 cycles, 1000 N load.

Figure 8: Abrasion wear results for coatings 2-5