Advanced Characterisation of Nanocomposite Coatings

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Abstract

Nanocomposite coatings are systems comprised of two or more phases. Such multiphase coatings are becoming increasingly important as they offer the possibility of tailoring the coating architecture and achieving exciting new properties. An understanding of the coating nanostructure is important to complete the classic processing-structure-properties relationship and expedite the development of novel systems. However, comprehensive structural and chemical characterisation of such nanostructured coatings remains a considerable challenge. In this paper, results on three nanocomposite coating systems are presented (Ti-Al-B-N, Ti-B-C and Cr-Cu-N). The use of XRD, TEM and XPS for phase identification, determination of the relative phase fraction, grain size and structural defects are described. The accordance (or not) of the phase composition and relative phase fraction with the equilibrium phase diagram for these systems is examined. Specific interesting features of the spectra and micrographs are interpreted and their nanostructural significance discussed. Correlations are made between the nanostructure and mechanical properties.

1. Introduction

Nanocomposite coatings are multiphase nanocrystalline based systems. The coatings can be deposited by physical and chemical vapour deposition (PVD and CVD) methods.

Nanostructuring and multiphase compositions leads to a greater flexibility in tailoring properties, enhanced mechanical performance [e.g.1-4], and the possibility to develop self-adaptive coatings for tribological applications [5].

To form a multiphase nanostructure, there needs to be a thermodynamic driving force for phase separation. Consequently, consideration of the phase diagram is an integral part of the coating design process. However, as vapour deposition techniques have rapid quenching rates, they are non-equilibrium processes. The formation of metastable phases and the presence of defective structure need to be identified for the process-structure-property relationship to be fully characterised.

To understand and improve the properties of nanocomposite coatings, characterisation of the coating chemical composition, phase composition and nanostructure are paramount.

The chemical composition can be determined using many techniques, such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), Rutherford backscattering spectrometry (RBS), energy dispersive X-ray analysis (EDX) etc. The nanocrystalline phase can be identified using diffraction methods, such as X-ray diffraction (XRD) or electron diffraction. Average grain sizes can be determined from analysing XRD peaks and applying the Scherrer formula or Warren-Averbach approach

and the nanocrystallite size and spatial distribution within the coating bulk can be studied using transmission electron microscopy (TEM). However, when the grain size drops below ≈ 1 nm, the XRD peaks become strongly broadened, resulting in the spectrum often being difficult to interpret. In such cases, the coating nanostructure is often termed 'X-ray amorphous'. Diffraction techniques offer little or no information on the presence or composition of phases in the coatings which are either X-ray amorphous or truly amorphous. The presence and composition of such phases generally needs to be determined by other techniques, the most useful being XPS, but some information is also obtainable using optical methods such as Fourier transform infra-red spectroscopy (FTIR) or Raman spectroscopy.

Diffraction techniques are also unable to provide information on the relative phase fraction, due to diffraction spectra being inherently non-quantifiable. As both nanocrystalline and amorphous phases can often be separately identified and the spectra easily quantified, XPS provides a good method for determining relative (atomic) phase fractions.

By reviewing the results of investigations into various coating systems undertaken by the author and his co-workers, this paper will describe how diffraction and electron spectroscopic techniques can be employed to give a reasonably comprehensive characterisation of the structure and relative phase fraction of nanocomposite coatings. Only a brief summary of the deposition conditions and mechanical properties of these coatings are given - full details are available in the references cited.

2. Experimental

Analytical results from three techniques will be presented, XRD, XPS and TEM. XRD spectra were recorded using a glancing angle XRD (GAXRD) instrument constructed in-house at an incident angle of 0.5° employing unmonochromated Cu radiation. A high-precision variable slit before the sample and Soller slit collimator between the sample and detector were used for angular resolution. A solid-state detector was employed to isolate the $K\alpha$ doublet and reduce background noise to a minimum. Grain sizes were determined by adopting the single line method described by Kiejser [6] based on the least-squares fitting of broadened peaks to a pseudo-Voigt function.

All XPS measurements were acquired at constant analyser energy. The Ti-Al-B-N coatings were analysed using a VG Sigmaprobe, employing an Al $K\alpha$ source and hemispherical analyser. A pass energy of 30 eV and step of 0.1 eV were used. For the Ti-B-C coatings, a Riber Nanoscan 50 was employed, with the MAC2 semi-imaging analyser set at an energy resolution of 0.5 eV and step of 0.1 eV. Both instruments were calibrated on the Cu $2p_{3/2}$ peak at 932.7 eV and the Au $4f_{7/2}$ peak at 84.0 eV. Surface hydrocarbon was used for charge referencing purposes, at a binding energy of 284.8 eV. Prior to analysis, the surface oxide was removed using a 3 keV argon ion beam. Curve fitting was performed after a Shirley background subtraction by non-linear least squares fitting of a mixed Gaussian/Lorentzian function. Quantification involved sensitivity

factors based on standard materials for the Riber Nanoscan 50 and transmission function modified Wagner sensitivity factors on the VG Sigmaprobe.

The TEM work was performed on a LaB₆ Philips CM200 operated at 200 keV. Plan-view specimens were prepared by thinning through the substrate, leaving the surface of the coating sufficiently thin for investigation. Final thinning was undertaken on a Gatan precision ion polishing system at an accelerating voltage of 5 keV.

3. Results

3.1. The Ti-B-N and Ti-Al-B-N Systems

Much work has been undertaken on the Ti-B-N and Ti-Al-B-N coatings systems. The equilibrium phase diagram for Ti-B-N has been given by Novotny et al [7]. For Ti-Al-B-N, this diagram can be modified to account for the known substitution of Al for Ti in the f.c.c. lattice of TiN, as shown in Fig. 1. Inspection of the phase diagram shows that the Ti-B-N and Ti-Al-B-N systems contain many interesting phases. Coatings deposited with compositions along the Ti(Al)N-TiB₂ and Ti(Al)N-BN quasi-binary sections and in the ternary Ti(Al)N, TiB₂, BN region have all been of particular interest to researchers.

A range of Ti-Al-B-N coatings were deposited by electron beam evaporation at a substrate temperature of 450 °C with nominal compositions lying on the (Ti,Al)N-BN

quasi-binary section [8]. The elemental compositions of these coatings measured by XPS are given in Table 1 and are marked as circles on the phase diagram in Figure 1. Knowing the coating stoichiometry, $(\text{Ti,Al})\text{B}_x\text{N}_y$, the phase compositions can be calculated from the following equations:

$$C_{\text{TiB}_2} = \frac{(1 + x - y)}{(1 + x + 2y)} \quad C_{\text{TiAlN}} = \frac{(2 - x + y)}{(1 + x + 2y)} \quad C_{\text{BN}} = \frac{(-2 + x + 2y)}{(1 + x + 2y)}$$

where x and y correspond to the B and N stoichiometry values respectively [9]. The calculated phase compositions are given in Table 1. According to the phase diagram, coating 1 should have a nominal phase composition of 42 % $(\text{Ti,Al})\text{N}$ and 57 % BN, with the $(\text{Ti,Al})\text{N}$ fraction increasing for the other coatings, up to 92 % for coating 5. In addition, a small fraction of TiB_2 may be expected in all coatings. The XRD spectra are presented in Figure 2. The only identifiable nanocrystalline phase present is f.c.c. $(\text{Ti,Al})\text{N}$. Thus, the BN phase must be assumed to be amorphous. For coatings 1-3, the $(\text{Ti,Al})\text{N}$ average grain size increases as the BN phase fraction decreases, as expected from competitive phase growth considerations. This trend does not continue for coatings 4 and 5, most probably due to the change in texture. Peak fitted XPS B 1s and N 1s core level spectra are shown in Fig. 3. The B 1s peak positions of 190.5 eV and 187.6 eV and N 1s peak positions of 396.9 eV and 397.9 eV are in good agreement with those expected for (BN and TiB_2) and $((\text{Ti,Al})\text{N}$ and BN) respectively [9]. To obtain a good peak fit of both the B and N 1s peaks, a third component is required, corresponding to sub-oxide species. A comparison of the relative phase fraction calculated from the phase diagram to that actually present in the coatings is given in Table 1. The agreement is good. This is

the case both for these Ti-Al-B-N and other Ti-B-N coatings which have a three phase TiB₂, TiN and BN composition [8-10].

The B 1s region for these Ti-Al-B-N coatings shows the emergence of a third peak at low binding energies for coatings with low B concentrations (Fig. 4). This peak has a binding energy of 185.9 eV and an unusually small FWHM. There is no B 1s peak listed with such a low binding energy in the NIST XPS database [11]. For inorganic compounds there is generally a good correlation between core level binding energy and electronegativity of the ligand. Consideration of the electronegativities and binding energies for various B ligands has enabled an extrapolation of the B 1s binding energy down to 185.9 eV [8]. For such a binding energy, a ligand with a Pauling electronegativity of approximately 1.6 would be expected. Ti has a Pauling electronegativity of 1.54. Interestingly, however, the binding energies of the Ti borides, TiB₂ and TiB, (and elemental B) occur at 187.9 ± 0.1 eV, i.e. at much higher binding energies than 185.9 eV [12]. These high binding energies result from the strong B-B bonding which exists in both TiB₂ and TiB. B-B bonding is reported to be significantly stronger than Ti-B and Ti-Ti bonding in both compounds [13,14]. The nature of the 185.9 eV peak thus corresponds to a local environment in which B atoms are locally bonded to Ti atoms, but are unable to form a B-B network. Within the nanocomposite structure, two possibilities arise (i) B atoms becoming entrapped within the (Ti,Al)N grains and substituting for N atoms within the (Ti,Al)N structure or (ii) B atoms located at the grain boundary between two (Ti,Al)N grains.

Mayrhofer et al have reported the formation of Ti(N,B) for B concentrations up to 17 at.% [15] and as argued above, the binding energy of 185.9 eV is consistent with the B atom existing in a local environment of many Ti atoms. Consequently, the most probable origin of this peak is B substituting for N in the (Ti,Al)N nanocrystallites. The small FWHM may be explained by a reduction in the solid-state phonon broadening caused by the absence of a 3-D periodic structure for the B atoms giving rise to this peak.

The mechanical properties of these TiAlBN coatings are good, with all coatings showing an improvement over commercial TiN and TiAlN in lubricated cutting tests [16]. The performance improved with increasing (Ti,Al)N content and coating 5, with a (Ti,Al)N content of 90 at.% showed a 2.5 fold increase in lifetime. The incorporation of a small percentage of B into (Ti,Al)N (less than 1 % of N atoms replaced by B for coating 5) has no adverse affect on the mechanical properties, on the contrary, age hardening is likely to occur at elevated temperatures [15].

3.2. The Ti-B-C System

For coatings which require a good resistance to sliding wear, there is an obvious benefit in reducing the friction coefficient. This can be achieved by combining hard and lubricant phases in a nanocomposite coating. The phase diagram for the Ti-B-C system shows the potential of depositing nanocomposite coatings comprised of a hard TiB₂ phase and a low-friction diamond-like carbon (DLC) phase (Fig. 5). Ti-B-C coatings were co-

sputtered from TiB₂ and C targets by magnetron sputtering at a substrate temperature of 150 °C [17]. The coating compositions determined by XPS are shown in Fig. 5. All of the coatings lie close to the TiB₂-C tie line, but a deficiency in B has resulted in their location within the TiB₂-TiC-C three phase region. The C concentration increases from 18 at.% in coating 1 to 90 at.% in coating 7.

GAXRD spectra for these coatings are presented in Fig. 6. The only nanocrystalline phase present is hexagonal TiB₂, there are no peaks indicating the presence of TiC. Grain sizes (determined from the (001) and (101) peaks) decrease from 9.5 nm at 18 at.% C to 1.9 nm at 61 at.% C. At higher C concentrations the coating is amorphous. The TiB₂ (001) and (002) peak positions shift to lower angles and the (100) to higher angles as the C concentration increases. XPS C 1s and B 1s spectra from coating 2 (39 at.% C) are shown in Fig. 7. The C peak is composed of two components (at 282.9 and 284.5 eV) and the B peak one component at 188.0 eV. No peak corresponding to TiC (binding energy 281.9 eV) was observed. The peak structure was similar for all coatings. The small peaks at higher binding energies correspond to C-O and B-O bonding.

The C component at 284.5 eV represents the DLC phase. The C component at 282.9 eV shows no shift in peak position with C concentration. However, the binding energy of the B 1s peak progressively shifts to higher values with increasing C content and for C contents of approximately 20-40 %, the XPS determined stoichiometry is Ti(B,C)_{2.0} [18]. Considering that the Pauling electronegativities of Ti, B and C are 1.54, 2.04 and 2.55 respectively and the peak positions for pure C and TiC are 285.5 and 281.9 eV

respectively, then the position of the C component at 282.9 eV is indicative of C bonding to both Ti and B. The three observations described above: (i) peak shifts of the (001) and (100) peaks in the XRD spectra; (ii) increase of the B 1s peak position with increasing C content; (iii) Ti(B,C)_x stoichiometry; are all consistent with the formation of a metastable Ti(B,C)_2 phase in addition to DLC.

Thus, a two phase $\text{Ti(B,C)}_2 + \text{DLC}$ coating has been deposited. In contrast to the Ti-B-N and Ti-Al-B-N coatings, these Ti-B-C coatings have a phase composition which is not in agreement with the phase diagram. However, Holleck and Lahres have predicted the formation of Ti(B,C)_2 for similar compositions at such deposition temperatures using phase field diagrams [19].

The free energy of formation, $^f\Delta G_{298}^0$, of TiB_2 is -317 kJ/mol, whereas that of graphite is 0 kJ/mol. $^f\Delta G_{298}^0$ of metastable Ti(B,C)_2 is likely to be somewhat similar to TiB_2 and $^f\Delta G_{298}^0$ of DLC will be very similar to graphite. Consequently, during film growth, there is a driving force for C to substitute into the hexagonal TiB_2 phase rather than forming a pure C phase. This results in the DLC phase forming only when there is excess C; i.e. when no more C can be accommodated in the Ti(B,C)_2 phase. A plot of DLC content vs. total C content has shown this to be the case [17,18].

The formation of Ti(B,C)_2 rather than TiB_2 is detrimental to the mechanical properties of these coatings. A friction reducing effect is observed only at total C concentrations above 50-60 at.%. Below this value, not sufficient lubricant phase was available, as increasing

C incorporation into the Ti(B,C)_2 phase caused the concentration of low-friction DLC phase to remain below < 15 at.%. Coating 5 (60 at.% C) offered the best combined hardness (20 GPa) and low-friction (< 0.2) properties [17].

3.3. The Cr-Cu-N System

Most protective coatings are ceramic compounds exhibiting a high hardness and elastic modulus. However, it is well known that a high H/E ratio is an indicator of good wear resistance for a wide range of materials [20]. Consequently, desirable properties for many coatings are a relatively high hardness combined with a relatively low elastic modulus (similar to that of the underlying metallic substrate) [21]. As grain size reduction leads to an inherent increase in hardness (the Hall-Petch effect), nanostructuring materials which are predominantly metallically bonded could lead to coatings with a sufficiently high hardness to offer good protection, high toughness and an elastic modulus similar to the substrate.

The equilibrium Cr-Cr phase diagram given in Fig. 8 shows only a small solubility of Cr in Cu [22]. Rebholz et al have shown that reactive sputter deposition of Cr can result in up to 16 at.% N being interstitially incorporated within the Cr phase as Cr(N) [23]. Cu does not readily form a nitride phase. Consequently, the design concept for these coatings was to deposit hardened Cr(N) nanocrystallites embedded within a minority amorphous matrix of Cu by reactive sputtering of Cr and Cu,. Five coatings were reactively co-

sputtered from Cr and Cu targets at a substrate temperature of 300 - 350 °C [3]. The Cr/Cu compositions are given in Fig. 7 (Cu content ranging from 2 - 55 at. %) and the N content across the range of coatings varied between 18 and 23 at. %. XRD spectra showed Cr-Cu-N coatings 1 to 3 (3 - 8 at. % Cu respectively) to contain two nanocrystalline phases - Cr(N) and Cr₂N.

Increasing the Cu content to 23 at. % (coating 4), gave rise to the most interesting nanostructure and mechanical properties. The XRD spectrum exhibited a single broad peak, providing little information on structure. However, a dark field TEM image was obtained using the overlapping α -Cr (110) and β -Cr₂N (200) reflections (Fig. 9). The nanocrystallite phase composition cannot be unambiguously determined from the electron diffraction pattern, but is probably a mixture of Cr(N) + Cr₂N. The nanocrystallite size is very fine and uniform; there is a strong preferential orientation of the nanocrystallites and their average grain size is approximately 2 nm.

Even at 23 at.%, Cu has not formed as a separate nanocrystalline phase. Considering the low solid state miscibility of Cr and Cu, very fine nanostructure and moderate deposition temperature, it may be expected that the majority of Cu atoms lie at grain boundaries. The Cu 2p_{3/2} peak position, at 932.7 eV (elemental Cu), is also in accordance with Cu cluster formation. Thus, a nanocomposite structure comprised of a Cr(N) + Cr₂N nanocrystalline component and a Cu amorphous component can be assumed.

In the general nanocomposite design proposed by Veprek [2], the critical concentration of amorphous phase required to achieve complete monolayer coverage of the nanocrystallites will vary with grain size. To assist in the understanding of the nanostructure forming in these coatings, hypothetical calculations have been undertaken to determine the critical concentration of Cu required for complete monolayer coverage of nanocrystalline Cr grains in an idealised *nc-Cr/a-Cu* structure. Calculations have been undertaken assuming the Cu monolayer to adopt one of two 2-D packing densities: simple square packing and hexagonal close packing. The actual packing density is probably random close packing, which would give rise to a packing density between these two ordered arrangements. A full description of this calculation is given in [3]. To summarise, for cubic shaped grains, the Cu concentration C_{Cu} (at.%) required for complete simple cubic packing monolayer coverage of Cr grains with a diameter, d , is given by:

$$C_{Cu} = \left(\frac{\pi r_{Cr}^3}{\pi r_{Cr}^3 + p d r_{Cu}^2} \right) \times 100$$

where r is the atomic radius (being taken as 0.125 and 0.128 nm for Cr and Cu respectively), and p is the packing density (e.g. 0.68 for b.c.c. Cr). For hexagonal close packing, the Cu concentration is given by:

$$C_{Cu} = \left(\frac{2\pi r_{Cr}^3}{2\pi r_{Cr}^3 + \sqrt{3} p d r_{Cu}^2} \right) \times 100$$

For a grain diameter of 3 nm, these equations give rise to Cu concentrations of 15.5 and 17.5 at.% for simple cubic and hexagonal close packing respectively. In Fig. 9, the mean value of the two packing densities (approximating to random close packing) is plotted as a function of grain size.

All nanocomposite systems will exhibit similar volume/surface area ratio effects as a function of grain size. From inputting a selection of different atomic radii (for different hypothetical systems), similar trends in the dependence of amorphous phase concentration with grain size are observed and the data fits well to either a power or logarithmic function for the different systems.

Although the results should clearly be treated as approximations, Fig. 9 suggests that ≈ 23 at.% Cu is sufficient for monolayer coverage in an $nc\text{-Cr}/a\text{-Cu}$ nanocomposite with a mean grain size of 2 nm (i.e. similar to coating 4). However, distinct preferential orientation of the nanocrystallites is observed for this coating, which would probably be promoted by incomplete rather than complete grain coverage. Consequently, the analytical results indicate that coating 4 has a nanostructure approaching that of $\alpha\text{-Cr(N)}$ + $\beta\text{-Cr}_2\text{N}$ separated by a Cu-rich amorphous grain boundary layer. However, the Cu may be clustered rather than forming a uniform monolayer.

The 23 at.% Cu coating performed best in reciprocating-sliding and impact wear tests. The impact resistance showed a factor of 3 improvement over the other CrCuN coatings and was more than 30 times better than single phase Cr(N) [3]. This enhanced wear

resistance can be attributed to a relatively high hardness (18 GPa) combined with excellent fracture toughness and adhesion to the substrate.

4. Conclusions

By presenting results on analytical investigations into Ti-Al-B-N, Ti-B-C and Cr-Cu-N coating systems, a combination of electron spectroscopic, microscopic and diffraction techniques has provided a reasonably comprehensive characterisation of the structure and phase composition of nanocomposite coatings. Phase diagrams are important in coating design, but the non-equilibrium vapour deposition process can often lead to deviations from structures predicted purely on this basis. Quantifying XPS spectra to yield relative phase fractions and careful interpretation of the spectroscopic and diffraction data to identify metastable phases or defective structure is essential for reliable process-structure-property relationships to be established. Nanocomposite coatings exhibit enhanced mechanical properties, but optimisation and further advances are dependent upon sound characterisation and a good understanding of the nanostructures formed.

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Figure and Table Captions

Table 1: Relative phase fractions for the TiAlBN coatings, calculated from the stoichiometry (*calc.*) and experimentally determined from curve fitting of the XPS B and N 1s peaks (*exp.*)

Figure 1: A modified Ti-B-N equilibrium phase diagram of Novotny et al [6] accounting for the known substitution of Al for Ti in (Ti,Al)N. The TiAlBN coating compositions are marked.

Figure 2: GAXRD spectra for the TiAlBN coatings, showing the presence of the f.c.c. (Ti,Al)N phase for all coatings. (Ti,Al)N grain sizes (G.S.) are indicated.

Figure 3: Curve fitted XPS B and N 1s peaks for the TiAlBN coatings

Figure 4: XPS B 1s peak for the TiAlBN coatings. Note the emergence of a new component at 185.9 eV as the B content is reduced

Figure 5: The equilibrium Ti-B-C phase diagram of Novotny et al [6]. The TiBC coating compositions are marked.

Figure 6: GAXRD spectra for the TiBC coatings. Grain sizes (G.S.) are given for the 18 and 61 at.% C containing coatings.

Figure 7: XPS C and B 1s peaks for coating 2

Figure 8: The equilibrium Cr-Cu phase diagram taken from Massalski et al [21]. The CrCuN coating compositions are marked.

Figure 9: (a) TEM plan view dark field image of CrCuN coating 5; (b) A higher magnification image of (a)

Figure 10: A plot of the atomic concentration of Cu required for monolayer coverage of Cr grains as a function of grain size in a hypothetical $nc\text{-Cr}/a\text{-Cu}$ nanocomposite coating. The Cu concentrations plotted are the mean value of those calculated for simple cubic and hexagonal close packing densities (approximating to random close packing).

Sample	Elemental				Relative Phase Fractions					
	Concentrations (at.%)				(Ti,Al)N		BN		TiB ₂	
	Ti	Al	B	N	<i>Calc.</i>	<i>Exp.</i>	<i>Calc.</i>	<i>Exp.</i>	<i>Calc.</i>	<i>Exp.</i>
1	10.1	11.4	29.1	49.4	42	46	57	52	1	2
2	16.8	9.0	26.4	47.8	50	55	47	42	3	3
3	25.3	10.1	16.0	48.6	70	-	29	-	2	-
4	36.2	8.0	6.2	49.5	88	88	11	11	1	1
5	39.1	7.2	4.2	49.5	92	90	7	8	1	2

Table 1

Figure 1

Figure 2

Figure 3

Fig. 4

Figure 5

Figure 6

Figure 7

Figure 8

(a)

(b)

Fig. 9

Fig. 10