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Development of modern analysis techniques for characterization and testing of coatings

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This paper presents some developments in methods and techniques for the analysis of deposited materials. These concern X-ray diffraction, electron probe microanalysis, X-ray photo-electron spectroscopy and soft X-ray emission spectroscopy.

1. Introduction

The aim of this paper is not to present a complete review of the state of the art in the analysis of deposited materials, but rather to show new developments, which are of general importance. Analysis techniques to be covered are X-ray diffraction, electron probe microanalysis (EPMA), X-ray photo-electron spectroscopy (XPS) and soft X-ray emission spectroscopy (SXRS). These techniques can be used to characterize deposited films with the ultimate goal of obtaining a better understanding of the process-structure-property relationships.

The analyses described will be illustrated using experience with CVD TiC layers on steels.

2. X-ray diffraction analysis of thin polycrystalline layers

A brief overview will be given of the possibilities of X-ray diffraction for the characterization of polycrystalline layers. Details can be found in textbooks¹. X-ray diffraction is non-destructive and averages over a reasonable, selectable volume (about 1 mm³) of the sample. Some information, for example that on lattice deformations and precise lattice parameters, cannot easily be obtained by other means. Because of diffraction geometries, only information about a fraction of crystallites is obtained. X-ray diffraction becomes increasingly accessible for non-specialists; for all X-ray diffraction analyses computer programs are commercially available.

2.1. Qualitative and quantitative phase analysis. The identification of phases in a layer, in its substrate or at the interface is of interest for the layer/substrate properties. Phase identification is based on the intensities and positions (=diffraction angles 2θ) of the diffraction maxima. Then spacings d follow from Bragg's Law: $2d \sin \theta = \lambda$, where λ is the wavelength of the X-rays. Since each compound has its specific set of d values and intensities, identification is performed by comparing the observed d with references like those of the JCPDS Powder Diffraction File.

Quantitative phase analysis is based on the intensity of a diffraction line, since this is proportional to the amount of material in a phase. In contrast to chemical analysis, X-ray diffraction gives the way and amount in which the chemical elements are combined in compounds.

Both qualitative and quantitative phase analysis may be less reliable if preferred orientation of crystallites occurs; also the sensitivity is influenced. It is difficult to account for texture (cf. 2.3.).

2.2. Chemical composition. Many phases show a range of compositions or can form solid solutions while their crystalline structure remains unchanged. Then the composition follows from the relation between lattice parameter and composition. If no data are available a first approximation is obtained in case of a solid solution of two components from Vegard's law:

$$d_x = x d_1 + (1 - x) d_2,$$

in which d_x , d_1 and d_2 are the spacings of the same lattice planes of the solid solution and both constituting phases and x is the mol fraction of phase 1 in the solution.

2.3. Preferred orientation (texture). The crystallites of polycrystalline layers often show preferred orientation. Most frequently fibre textures occur: a crystallographic direction predominantly coincides with the substrate normal. The fraction of the crystallites showing preferred orientation and the sharpness of the orientation distribution usually varies with growth circumstances. Because properties are anisotropic it is important to know the texture. Methods for measuring and representing textures are reviewed in refs 2 and 3. For CVD TiC layers on steels mostly a 110 fibre texture is observed; sometimes a weak secondary fibre texture may occur.

2.4. Long-range internal stresses (residual stresses). Stresses can be determined from changes in lattice spacings^{3,4}. Stresses may lead to deformation of the layer or the substrate, or to chipping off of the layer.

Mostly a biaxial state of stress occurs with a zero stress perpendicular to the sample surface. Then the spacings of planes inclined to the sample surface by ψ (Figure 1) and the stress in the direction ϕ are related by

$$(d_{\phi,\psi} - d_0)/d_0 = S_1(\sigma_1 + \sigma_2) + \frac{1}{2} S_2 \sigma_\phi \sin^2 \psi \quad (1)$$

or to a very good approximation:

$$(d_{\phi,\psi} - d_{\phi,\psi=0})/d_{\phi,\psi=0} = \frac{1}{2} S_2 \sigma_\phi \sin^2 \psi \quad (1a)$$

Figure 1. Definitions of angles ϕ and ψ as used in texture and stress analyses.

where $d_{\phi,\psi}$ is the spacing in the ϕ, ψ direction, d_0 is the strain-free spacing, S_1 and $\frac{1}{2} S_2$ are the so-called X-ray elastic constants, σ_1 and σ_2 are the principal stresses (Figure 1) and $\sigma_\phi = \sigma_1 \cos^2 \phi + \sigma_2 \sin^2 \phi$. From equation (1) it follows that $d_{\phi,\psi}$ vs $\sin^2 \psi$ yields a straight line, from which intercept and slope $\sigma_1 + \sigma_2$ and σ_ϕ follow. If d_0 is not known equation (1a) is used. A straight line is not always found in practice, e.g. with texture or stress gradients⁴.

For CVD TiC layers on steels equation (1) holds. The stresses can be explained quantitatively from the difference in thermal expansion—including phase transformations—between layer and substrate during cooling from deposition to room temperature.

Generally the composition, and therefore d_0 (cf. 2.2), of TiC is not known in advance. For the above mentioned TiC layers σ_ϕ proved to be independent of ϕ , i.e. $\sigma_1 = \sigma_2$. From equation (1) it then follows that $d_0 = d_{\phi,\psi}$, where ψ_0 obeys $\sin^2 \psi_0 = -4S_1/S_2$. The carbon content of TiC was then determined using the relation between lattice parameters and composition (cf. 1.2).

The so-called $\sin^2 \psi$ method not only provides stresses but also strain-free lattice spacings. Furthermore with X-ray diffraction stresses in the substrate can be measured without removing layers.

2.5. Crystallite size and non-uniform microstrains. From the broadening of diffraction maxima information is obtained about the imperfect crystalline structure¹⁻⁵ in terms of crystallite size and lattice deformation.

These may incorporate contributions from stacking faults, microtwins, concentration variations and stress gradients. Much information is needed to sort out all effects. Essential for line-broadening analysis is the elimination of the broadening by the instrument and the X-ray spectrum. Therefore a reference sample is required which shows no—or a known amount of—structural broadening. Using either breadth measures (integral breadth and half width) or Fourier coefficients for the description of profiles, corrections for the broadening measured with the reference sample can be performed. From the resulting breadth measures or Fourier coefficients an effective crystallite size and microstrain can be determined.

A simple and quick method⁵ uses breadth measures and the assumption that all line profiles concerned are Voigt functions, i.e. a convolution of Gaussian and Cauchy functions. Then β^c , the integral breadth of the Cauchy part of the profile only due to imperfectness, is interpreted as caused by finite crystallite size and β^g , the Gaussian part, is interpreted as caused by microstrains:

$$\beta^c = \frac{k\lambda}{D_r \cos \Theta} ; \beta^g = 4 e \tan \Theta \quad (2)$$

where k is a constant, D_r the effective crystallite size and e an average microstrain. This method uses a single line and is useful in comparing samples. More accurate methods, like the Warren-Averbach method, use more than one order of reflection of the same lattice plane⁶. Marked differences between size and strain values obtained by X-ray diffraction and by other techniques may occur; they can be explained quantitatively from differences in sampling and averaging implied by the methods used⁵.

For CVD TiC layers on steels the crystallite size was almost independent of the carbon content of substrate and gas phase (CH_4). The microstrain increased with increasing carbon content of the substrate and without CH_4 in the gas phase the microstrains were higher than with CH_4 .

3. Electron probe microanalysis

There are many problems in quantitative electron probe microanalysis (EPMA) of light elements^{7,8}. Finding correct solutions generally requires a lot of experience. In this section we will concentrate on new developments in the EPMA of light elements in surface layers.

A grossly neglected problem in the EPMA of light elements since Weisweiler⁷ recognized it as such in 1975, is the fact that intensity measurements of light elements have to be performed in an integral fashion. Their intensities cannot be determined by measuring at the maximum of the emission peak, because the shape of these emission lines is directly dependent on the nature of chemical bonding. Neglecting this can lead to errors in the order of 30–50%, depending on the type of standard used⁸. However, integral determination of emission lines requires long and tedious measurements. This problem was solved by the introduction of so-called area/peak (A/P) factors, which represent the ratio between the (true) area k -ratio and the peak k -ratio. For an extensive series of binary borides, carbides and nitrides these A/P factors have been determined^{8,9}. So, future light element analyses of these compounds can be simply carried out by measuring the maximum of the emission peak, after which the peak k -ratio can be converted into the area k -ratio using the A/P factor. In case of titanium carbide the A/P factors for C-K α radiation were also measured as a function of composition; they showed a very slight dependence on composition (see Figure 2).

In the area of matrix correction procedures for EPMA there are many new developments, partly connected with light element determinations^{11–14}. Until very recently the major problem in this field was the lack of a file of reliable light element analyses

Figure 2. Area/peak factors for carbon-K α radiation relative to Fe_3C for a number of compositions inside the homogeneity region of TiC.

on which correction programs could be tested. A considerable effort has been (and is being) made in this field by Bastin and coworkers^{9,13}. Measurements for boron and carbon have been completed, for nitrogen work is in progress.

In correction procedures for light element determinations the correction for matrix absorption effects no doubt represents the major part. Workers in this field are mainly hampered by the fact that the mass absorption coefficients (MAC's) for light elements are known with little accuracy. Attempts are now being made to produce new sets of consistent MAC's based on light element test files¹⁰.

In the composition measurements of TiC coatings (deposited by CVD) another special problem had to be solved. This was caused by the presence of iron and chromium containing impurities in the TiC layer, probably (Fe, Cr)₃C precipitates. They were mostly present near the substrate-coating interface in particles of 0.1–1 μm in diameter (see Figure 3). The carbon measurement by EPMA in these TiC coatings is hindered in two ways:

(a) the Cr-L α X-ray emission line (2nd order) coincides with that of carbon-K α , so that the calculated carbon concentration is slightly too high;

(b) the A/P factor for C-K α radiation of carbides like (Fe, Cr)₃C is clearly different from that of pure TiC⁹.

The solution to (a) was: subtract the Cr-L emission spectrum of a pure chromium standard (multiplied by the calculated *k*-ratio for Cr-L) from the C-K α emission spectrum measured in TiC and compare this with the original C-K α spectrum in Fe₃C as a standard. For the chromium concentrations observed in TiC (between 1 and 4 at %) the effect of Cr-L emission on the measured C-K α emission proved to be very small. The remedy for problem (b) was simple: the A/P factors for parts of TiC coatings where the (small) precipitates of other carbides were clearly visible had to be determined by recording the complete C-K α emission spectrum. A considerable change of A/P factor was found: on the average for TiC containing precipitates A/P = 0.87 ± 0.02 , whereas for pure TiC standard A/P = 0.73 ± 0.01 .

In parts of coatings containing no precipitates the A/P factor did not change significantly from that of pure TiC.

Having solved all these problems¹⁵ the composition of TiC coatings (deposited by CVD) could be determined very

Figure 4. Composition of CVD-grown TiC (measured by EPMA at the centre of the coating) in relation to substrate composition.

accurately¹⁶, see Figure 4, where the average composition measured at the centre of the coating was found to range between 46 and 47.5 at % carbon, almost independent of the substrate composition. An explanation for this phenomenon has been presented elsewhere¹⁶.

4. XPS and SXRS

The electron binding energies in materials can be studied by several spectroscopic techniques, X-ray photo-electron spectroscopy (XPS) and soft X-ray spectroscopy (SXRS) being the most important ones¹⁷. Complementary to these techniques are measurements of X-ray absorption spectra¹⁸, e.g. using the extended X-ray absorption fine structure (EXAFS). An important application is in the study of bonding states in surface layers in relation to their composition.

We illustrate this for the case of TiC wear-resistant coatings. To study the material TiC over its broad composition range, a dozen samples were prepared by melting mixtures of the elemental powders using arc-melting techniques. The resulting polycrystalline TiC contained less than 0.2 wt % oxygen and 0.1 wt % nitrogen (as measured by LECO TC 136 instrumentation, (see Acknowledgement). After the determination of lattice constants and compositions of the samples¹⁶, we subjected them to XPS and SXRS techniques. The energy of the Ti-2p_{3/2} level, which is involved in the bonding between titanium and carbon, was measured by XPS (using MgK $\alpha_{1,2}$ radiation; all values were determined relative to the Au-4f_{7/2} level). The resulting curve (Figure 5) shows a non-linearity in the binding force between titanium and carbon with a maximum binding energy for TiC containing about 44 at % carbon. These findings were confirmed by SXRS (using the electron microprobe) of TiC developed in a diffusion couple Ti/TiC(+C). The intensity ratio of the Ti_{L₁} = Ti_{L_m} emission line in TiC and in pure Ti as function of TiC composition is shown in Figure 6. The shape of this emission band is reflecting the band structure of the material¹⁸. XPS and SXRS measurements on TiC coatings grown by CVD (having an almost constant composition, see above) show similar XPS and SXRS results.

It is interesting to note that the observed maximum in binding energy (Figure 5) is coinciding (within experimental accuracy) with the TiC composition having the maximum lattice parameter¹⁶ and the maximum melting point¹⁹. This leads us to the conclusion that in our CVD experiments a preferential

Figure 3. X-ray composition image of a CVD-grown TiC coating showing (Fe, Cr)₃C precipitates near the substrate/coating interface (white dots: precipitates). The white bar represents 10 μm .

Figure 5. Binding energy of the Ti-2p_{3/2} level in polycrystalline TiC vs composition.

Figure 6. $J(\text{Ti-L}_{\eta}/\text{L}_1)$ in TiC vs carbon composition in TiC, $J(\text{Ti-L}_{\eta}/\text{L}_1)$ in Ti as determined by SXRS (J =intensity).

composition was formed, with a maximum in binding energy, which is thermodynamically the most stable, and which probably contains a minimum of lattice vacancies (maximum lattice constant). The implications this could possibly have for the monitoring of physical properties of CVD-grown TiC by changing its composition have already been discussed¹⁶.

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