

Structure and Properties of Surface Layers: X-ray Diffraction Studies*

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Abstract

Because X-rays are strongly absorbed on propagation through solid material, X-ray diffraction analysis can be fruitfully applied in the study of surface layers. After a brief discussion of some aspects of X-ray diffraction analysis of surface layers, attention is focussed on investigations of stress development and interdiffusion in surface layers. The behaviour of surface layers depends largely on their state of (residual) macro- and microstress. The development and possible relaxation of macrostress in surface layers can originate from the thermally imposed difference in shrink or expansion between layer and substrate, from developing concentration profiles and from structural changes, in particular phase transformations. Diffusion processes in multilayers, composed of alternately stacked sublayers of elements A and B, are highly affected by the multitude of interfaces and therefore differ from those in bulk material. The effective diffusion coefficients can be determined from the decrease of the intensity of the reflections corresponding to the composition-modulation period [so-called (000) satellites], and the change of the integrated intensities of reflections from produced or retained crystalline components. Examples of interdiffusion in an amorphous multilayer (in conjunction with structural relaxation) and in a crystalline multilayer (leading to amorphisation) are presented.

1. Introduction

Great interest exists in finding and understanding the relation between structure and properties of surface layers. Strong stimuli for fundamental research originate from promising or already successful technological applications of 'surface engineering'. Properties of surface layers can be significantly different from those known for bulk materials as illustrated by the following remarks:

- (i) Surface layers are normally subjected to internal stresses. These bear a close relation to the occurrence and kinetics of recrystallisation and phase transformations and (also thereby) to the mechanical strength and the corrosion resistance.
- (ii) Internal and external interfaces are 'associated' with a significant fraction of all material in the surface layer. Interfaces can play an important role in diffusion processes by allowing short-circuit diffusion and by enhancing the contribution of the so-called gradient energy attributable to composition gradients.

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- (iii) Surface-layer/substrate assemblies should be conceived of as composites. The presence of the surface layer has consequences for the properties of the substrate. If stresses occur, the constraint of mechanical equilibrium imposes a state of stress in both the layer and the substrate, influencing the solid-state chemistry (notably solubilities and precipitation behaviour).

The development of new bulk materials, with properties meeting demands more severe than before, can be an extremely costly enterprise. In many cases only the surface region of a workpiece is subjected to external loads (e.g. corrosive agents and stress in rotating-bending fatigue). This explains, from a technological point of view, the growing interest in treatments bringing about an upgrading of the surface-adjacent material of workpieces. Relatively *thick* surface layers (at least a few μm) are of interest, for example:

ceramic coatings produced by chemical or physical vapour deposition for enhancing the wear and corrosion resistance (TiC and TiN coatings on steel);

surface layers modified by chemical interaction between an active component of a gaseous, salt-bath, powder or plasma medium and a component of the substrate (nitriding, carburising and boriding of steels);

surface layers of the substrate modified by mechanical deformation, melting and solidification, and phase transformations (shot-peening, laser and induction hardening).

The practical interest for relatively *thin* surface layers (100 nm or less) can largely be ascribed to developments in the microelectronic industry, for example:

thin crystalline metalsilicide layers produced by interdiffusion in a multilayer composed of alternately deposited (e.g. by sputtering) metal and silicon layers (metalsilicides such as MoSi_2 , TiSi_2 and WSi_2 are considered as alternatives for doped polycrystalline silicon in a new generation of integrated circuits: Very Large Scale Integration).

Further, a recent finding (Schwarz and Johnson 1983) hints at the possible production of bulk amorphous metallic alloys by diffusion in an aggregate of well chosen crystalline components. This process can be studied successfully in a thin layer aggregate, for example:

a multilayer composed of alternately stacked layers of Ni and Ti can (partly) be transformed in an amorphous NiTi alloy by annealing.

Because X-rays are strongly absorbed on propagation through solid material, X-ray diffraction analysis should be considered as a surface-sensitive method. There is perhaps no other method for probing surface-adjacent material meeting the versatility of the X-ray diffraction method (phase detection and identification; determination of composition and of lattice imperfections as internal macro- and microstresses and crystallite sizes, preferred orientation, layer thickness). The advent of computers and commercially available software allows application on a routine basis.

This paper is not intended to be a survey of current X-ray diffraction methods for the analysis of surface layers; a recent review has been provided by Delhez *et al.* (1987). Rather, our intention is to demonstrate the kind of fundamental physical-chemical knowledge about surface layers that can be acquired by X-ray diffraction analysis.

The *development of stress* in surface layers is only fragmentarily understood. In particular, if accommodation of misfit can occur (leading to stress relaxation), only

scattered data relevant to specific materials can be found in the literature. The challenge is to find out those operating mechanisms that have general significance and lend themselves to modelling (Section 3).

Fundamental aspects of *solid-state diffusion*, at present insufficiently grasped, can be studied by employing thin film systems in particular. Very small diffusion coefficients can be measured because diffusion distances are small. Effects due to gradients of both concentration and stress can be analysed using artificially layered composites. Microstructural changes induced by diffusion lead to time-dependent diffusion coefficients (Section 4).

2. Remarks on X-ray Diffraction Analysis of Surface Layers

(a) Measures for X-ray Penetration

The depth of penetration of X-rays plays an important role in the analysis of surface layers, in particular if gradients of stresses, composition and microstructure occur. In quantifying the penetration of X-rays into a specimen in a powder diffractometer, an absorption factor is used:

$$A = \exp(-\mu k z), \quad (1)$$

where μ denotes the (effective) linear absorption coefficient and k is a trigonometric function determined by the diffraction geometry. For ω tilt performed about the $\theta/2\theta$ axis, we have

$$k = 2 \sin \theta \cos \omega / (\sin^2 \theta - \sin^2 \omega). \quad (2a)$$

For ψ tilt performed about an axis which lies in the specimen surface and is perpendicular to the $\theta/2\theta$ axis, we have

$$k = 2 / \sin \theta \cos \psi. \quad (2b)$$

The integrated intensity dP , i.e. the number of counts observed from a layer of thickness dz at depth z below a surface, is given by

$$dP = CA dz = C \exp(-\mu k z) dz, \quad (3)$$

where C depends on the diffraction geometry. Hence, the total integrated power from a surface layer of thickness t is given by

$$P(t) = C \{1 - \exp(-\mu k t)\} / \mu k = P_\infty \{1 - \exp(-\mu k t)\}. \quad (4)$$

On this basis four different measures for penetration can be defined (Delhez *et al.* 1987) as follows: The *penetration depth* ζ_r is the depth where the ratio $dP(z=\zeta_r)/dP(z=0)$ equals an arbitrarily chosen fraction r :

$$\zeta_r = \frac{1}{\mu k} \ln \frac{1}{r} \quad (0 < r < 1). \quad (5a)$$

The *information depth* ζ_i is the intensity-weighted average depth; for a layer of total thickness t it follows from

$$\zeta_i(t) = \int_0^t z A \, dz / \int_0^t A \, dz = \frac{1}{\mu k} - \frac{t \exp(-\mu k t)}{1 - \exp(-\mu k t)}. \quad (5b)$$

The *contributing thickness* τ_R of a diffracting surface layer of total thickness t is the thickness for which the ratio $P(z=\tau_R)/P(z=t)$ equals an arbitrarily chosen fraction R :

$$\tau_R(t) = \frac{1}{\mu k} \ln \left(\frac{1}{(1-R) + R \exp(-\mu k t)} \right) \quad (0 < R < 1). \quad (5c)$$

The *equivalent thickness* τ_{eq} is the thickness of a hypothetical non-absorbing layer giving the same amount of diffracted intensity as the actual absorbing layer of total thickness t :

$$\tau_{eq}(t) = \frac{1}{\mu k} - \frac{\exp(-\mu k t)}{\mu k}. \quad (5d)$$

It follows for an infinitely thick layer that

$$\zeta_i(t=\infty) = \tau_{eq}(t=\infty) = 1/\mu k, \quad (6a)$$

and, in the case that $r = 1/e$ and $R = (e-1)/e$,

$$\zeta_{r=1/e} = \zeta_i(t=\infty) = \tau_{R=(e-1)/e}(t=\infty) = \tau_{eq}(t=\infty) = 1/\mu k. \quad (6b)$$

The parameter most frequently used in the literature to account for absorption is $1/\mu k$. Equation (6b) shows that it can be interpreted in various ways.

In general, for the characterisation of absorption effects a depth or thickness parameter should be selected dependent on the kind of information to be extracted from the diffraction experiment; for example, a stress value should be related to a depth. Obviously, for the analysis of surface layers a measure for penetration dependent on t should be adopted and, considering the arbitrary choice of r or R as a disadvantage, the measures ζ_i and τ_{eq} are to be preferred. It should be noted, that these measures also have a well-defined meaning for infinitely thick specimens.

The information desired determines the radiation (i.e. wavelength) to be applied. If lattice-spacing gradients occur in a surface layer, the depth analysed in a diffraction experiment should be as small as possible, implying utilisation of radiation which is absorbed relatively strongly; in this case the spacing-depth profiles can be determined by successive layer removal (e.g. by polishing). On the other hand, if a substrate beneath a coating should be analysed, this may be achieved without removal of the coating by applying radiation which is absorbed relatively weakly in the coating.

(b) Intensities

Integrated intensities and peak intensities observed for thin coatings are smaller than those for infinitely thick specimens of the same material, as is immediately seen from equation (4). This simple equation can be applied to normalise data from thin coatings; for example, for the quantitative comparison of the degrees of preferred orientation of the crystallites in various coatings of different thicknesses.

(c) Peak Position

Peak positions are used to identify phases, to determine the composition of solid solutions and to measure macrostress. If composition and/or macrostress change significantly within the depth probed by the X-rays, the peak position observed yields the lattice spacing $\langle d \rangle$, an intensity-weighted average,

$$\langle d \rangle = \frac{\int_0^t d(z) \exp(-\mu k z) dz}{\int_0^t \exp(-\mu k z) dz}. \quad (7)$$

It can be shown that $\langle d \rangle$ is a very good approximation for the lattice spacing at depth $z = \zeta_1(t)$. A more detailed discussion of equation (7) is given elsewhere (Delhez *et al.* 1987).

(d) Composition Profile Analysis in Thick Layers

A lattice-spacing profile can be traced by X-ray diffraction analyses after successive sublayer removals, if the effective X-ray penetration is significantly smaller than the extent of the lattice-spacing profile (see also Section 2e). After each sublayer removal some average lattice spacing is extracted from the diffraction data and assigned to some location [see text below equations (6b) and (7)] in the layer. The resulting spacing-depth profile can be transformed into a concentration-depth profile if the relation between lattice parameter and composition is known (in many cases a linear equation will satisfy). For practical situations the following remarks are made: (i) successive sublayer removals could optimally be made in steps of the order of the depth analysed in the diffraction experiment; (ii) a correction for line shift by residual macrostress is usually necessary.

(e) Stress Analysis

A pragmatic division of the types of stresses/strains which can be found in crystalline material involves the distinction between: *macrostrain/stress*, which is homogeneous over macroscopic distances and is related to a change of the average lattice spacing (associated with line shift); and *microstrain/stress*, which changes over distances of the order of one lattice spacing and is related to variations of the lattice spacing with respect to the average value (associated with line broadening).

A state of plane stress, characterised by two principal stresses σ_1 and σ_2 parallel to the surface, can usually be assumed for surface layers (often $\sigma_1 = \sigma_2 \equiv \sigma_{\parallel}$). The established $\sin^2\psi$ method for the determination of macrostress is based on the dependence of the lattice spacing of a specific set of lattice planes (hkl) on tilt angle ψ or ω [depending on the goniometer employed; cf. equations (2)] with respect to the surface normal. (This implies that for a polycrystalline specimen at different settings of ψ or ω other grains diffract.) If the (X-ray) elastic constants are known a value for the strain-free (reference) lattice spacing is obtained together with a value for the stress. This allows simultaneous determination of composition and stress depth profiles by consecutive sublayer removals, provided no appreciable composition and stress gradients occur over the depth of penetration of the X-rays. In general the presence of composition and stress gradients in the diffracting volume and the occurrence of preferred orientation require a dedicated approach in the stress analysis (Hauk and Macherauch 1983).

In surface layers a sharp fibre texture often occurs with the fibre axis parallel to the surface normal. Then, if the selected reflection is only measurable for a very narrow ψ

range, application of the $\sin^2\psi$ method is impossible. Then two alternative routes are possible: (i) $\{hkl\}$ lattice planes may be selected such that different members of the $\{hkl\}$ family diffract during ψ tilt at different ψ ; (ii) different $\{hkl\}$ reflections may be combined in one $\sin^2\psi$ analysis. In these cases the calculation of so-called X-ray elastic constants should be performed taking into account (i) anisotropic elastic behaviour of the crystals, (ii) crystal interaction *and* (iii) distribution of crystal orientations.

Line broadening* due to microstresses can be interpreted in two essentially distinct and extreme ways. A specimen could be composed of crystals each of constant but different lattice parameter(s) and it could be composed of crystals each exhibiting a lattice-spacing distribution along the diffraction vector. The line broadening by the first type of specimen is thought to correspond with incoherent diffraction by the constituent crystals. The line broadening by the second type of specimen is thought to be dominated by coherent diffraction of the material within a crystal. Additional information is required for unambiguous interpretation of 'strain broadening'.

In common practice one restricts stress analysis to the determination of the (residual) macrostress and one usually tends to ignore the microstrains. It can be shown that for an understanding of material behaviour, often the combined effects of both macro- and microstrains should be considered.

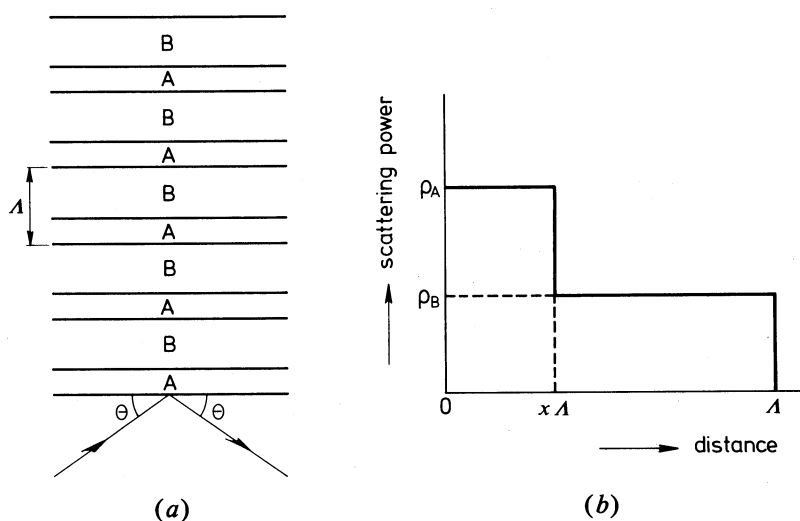


Fig. 1. (a) Schematic presentation of a multilayer composed of alternately stacked layers of materials A and B. Because of the composition modulation with period A , the multilayer can be conceived of as a one-dimensional crystal which, for the diffraction geometry indicated, can give rise to diffraction maxima (see equation 8). (b) Distribution of scattering power (schematic) within the unit cell of length A describing the composition modulation. Layers A and B are supposed to be of constant composition.

* Line broadening originates from the imperfection of the microstructure of the specimen, from the instrument and from the X-ray spectrum used. Methods exist to extract the contribution from the imperfection of the microstructure. It is common practice to interpret this contribution (structural line breadth) in terms of microstrains and of smallness of size of the diffracting crystallites (Delhez *et al.* 1982).

(f) *Analysis of Diffraction by Multilayers*

At present there is great interest in the investigation of multilayers, as for example prepared by alternately depositing layers of component A and component B. If the A and B layers are of constant thickness the layered structure can be conceived of as a one-dimensional crystal characterised by the periodicity Λ (the composition-modulation period; see Fig. 1a). The magnitude of the modulation period is at least a few atomic diameters. Consequently, 'Bragg maxima' can occur for (very) low values of 2θ . The m th order maximum is denoted as the $(00m)$ reflection. These maxima occur even when the sublayers are amorphous (see Section 5)!

The effect of refraction on line position is important at low angles of diffraction. Within the framework of the kinematical diffraction theory, for multilayers a modified form of Bragg's law can be derived (cf. Wilson 1963):

$$(m\lambda)^2 = 4\Lambda^2(\sin^2\theta_m - 2\delta + \delta^2), \quad (8)$$

where θ_m corresponds to the observed position of the m th order reflection, λ is the wavelength used and $1 - \delta$ equals the real part of the volume-averaged refractive index. This equation can also be obtained in a straightforward way from the dynamical diffraction theory. From a plot of m^2 versus $\sin^2\theta_m$, values for Λ and δ are obtained. The average composition of the multilayer can be estimated from δ (cf. Miceli *et al.* 1986).

The composition profile (in the one-dimensional unit cell of the multilayer) may be determined by comparison of the diffraction pattern calculated for an assumed composition profile with the experimental data. This fitting procedure can be a very sensitive operation as is shown below.

Consider a multilayer composed of alternately stacked layers A and B and define a one-dimensional unit cell of period Λ comprising one A layer and one B layer with an interface at the fractional position x (Fig. 1b). For the sake of simplicity the kinematical diffraction theory is utilised; this does not affect the conclusions reached. If the diffraction phenomena are governed by the change in scattering power at the A/B interface (thus ignoring variations in scattering power within each layer), it follows for the structure factor F that

$$FF^* = (\rho_A - \rho_B)^2 \frac{\sin^2 \pi mx}{\pi^2 m^2}, \quad (9)$$

where the scattering powers ρ_A and ρ_B are proportional to the atomic scattering factors of atoms A and B. Clearly, for increasing order of reflection m , FF^* decreases roughly proportional to $1/m^2$.

Now the effect of a small change Δx of the A/B interface is considered, and then

$$\Delta FF^*/FF^* = 2\pi m \cot(\pi mx) \Delta x. \quad (10)$$

A change of the interface position as small as 25×10^{-4} already can induce large changes, of the order of 10%, in the intensities of the reflections (Fig. 2); note in particular that intensities of adjacent orders of reflection can change in opposite directions (Fig. 2a versus Fig. 2b). The sensitivity suggests determination of interface locations with an accuracy of better than one atomic diameter.

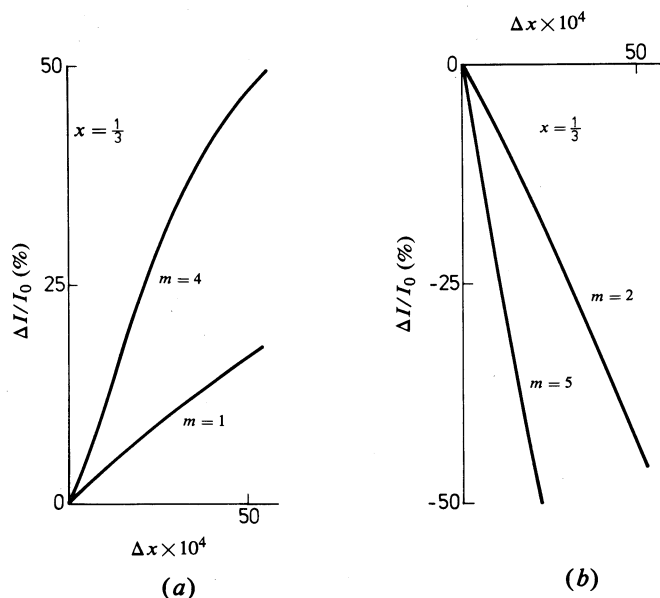


Fig. 2. Relative change of the squared modulus of the structure factor, and thus intensity $\Delta I/I_0$, of $(00m)$ multilayer reflections as a function of the shift Δx of the A/B interface in the unit cell (see Fig. 1b):

$$\Delta I/I_0 = \{FF^*(x+\Delta x) - FF^*(x)\} / FF^*(x),$$

where FF^* is given by equation (9). Calculations have been performed for $x = \frac{1}{3}$, which implies an unshifted interface at $A/3$, and for (a) $m = 1$ and 4 and (b) $m = 2$ and 5.

However, in practice measured diffraction patterns cannot be matched completely with calculated ones. For multilayers which are thought to possess a stepped composition profile in the unit cell as in Fig. 1b, a satisfactory fit for in particular the higher orders is not achieved. This may be due to inadequacy of the model adopted for the actual structure of the multilayer: variations in the unit cell composition profile and in A , which are difficult to account for. At present no straightforward procedure exists for investigation of diffusion processes in multilayers by comparison of calculated and measured diffraction patterns (cf. Hollanders and Thijssse 1988).

Finally, artefacts of the diffraction experiment may hinder accurate quantification. As compared with diffraction at high angles, diffraction at low angles (i) is much more sensitive to (local) curvature of the specimen and (ii) can suffer from inappropriate sampling in reciprocal space by beam divergence.

In the above the kinematical diffraction theory was used for the purpose of illustration. In many cases the kinematical diffraction theory (without or even with taking into account absorption within the one-dimensional unit cell) will be unsuited for a quantitative description of the $(00m)$ reflections; then a more rigorous (dynamical) diffraction theory is required.

3. Development and Relaxation of Macrostress

Residual (internal) stresses occur when separate portions of a specimen tend to assume different volumes, a process counteracted by cohesive forces. By their nature

residual stresses persist in the absence of an external load and are self-equilibrating. Two common origins of internal stress in surface layers are (i) the differences in thermal expansion/shrink between phases present in the layer/substrate composite and (ii) the presence of concentration profiles.

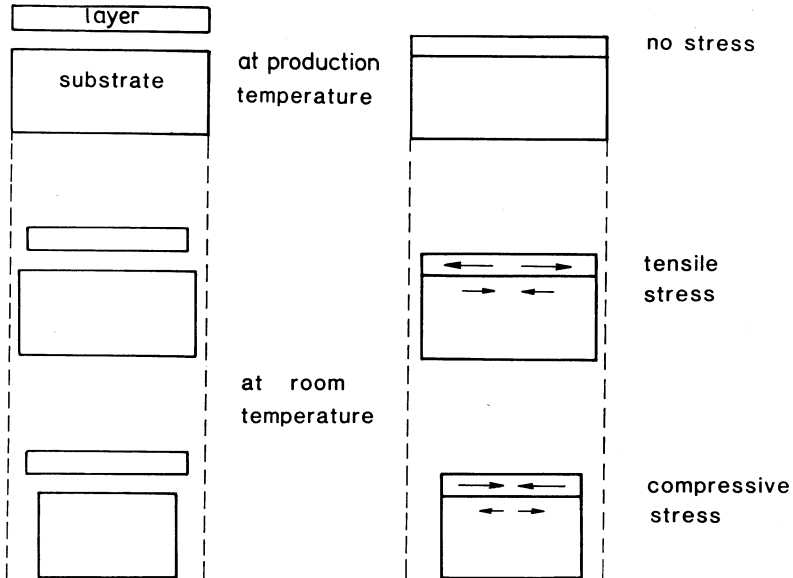


Fig. 3. Residual stresses in layer and substrate after cooling from the temperature where the layer was produced. At the production temperature, layer and substrate are assumed to be strain free. The difference in thermal expansion between layer and substrate and the imposed matching at their interface leads to stresses in layer and substrate of opposite sign.

(a) Inhomogeneous Thermal Behaviour and Stress

If, for example, after cooling from the temperature where the surface layer was produced, the lateral equilibrium dimensions of surface layer and substrate do not match, a lateral and linear misfit occurs and a state of stress can develop (Fig. 3). In this case modelling is relatively easy if complete elastic accommodation occurs.

Assuming that no strains develop during layer production, a quantitative prediction of the strain parallel to the specimen surface $\epsilon_{\parallel}^{\text{th}}$ in the surface layer can be obtained from the difference in thermal shrinkage between layer and substrate due to cooling from production temperature to room temperature. The layer is usually very thin compared with the substrate. Then, according to a simple model based on elastic behaviour, mechanical equilibrium, and a homogeneous stress distribution in both layer and substrate, it follows that the difference in thermal shrinkage between layer and substrate will be predominantly assimilated by the layer.

In general, the 'thermal strain' $\epsilon_{\parallel}^{\text{th}}$ parallel to the surface in a layer/substrate composite, of plate geometry with infinitely large lateral dimensions, after cooling from temperature T_0 to temperature T_a where the stress measurement is performed,

is given by

$$\epsilon_{\parallel}^{\text{th}}(T_a) = \int_{T_0}^{T_a} \{\alpha_{\text{sub}}(T') - \alpha_{\text{lay}}(T')\} dT', \quad (11)$$

where $\alpha_{\text{sub}}(T')$ and $\alpha_{\text{lay}}(T')$ are the thermal expansion coefficients at temperature T' of the substrate and layer respectively, including the effect of possible phase transitions. If practically all strain is accommodated by the layer (see above), it follows for the stress $\sigma_{\parallel}^{\text{th}}$ in the layer that

$$\sigma_{\parallel}^{\text{th}}(T_a) = \frac{E}{1-\nu} \epsilon_{\parallel}^{\text{th}}(T_a), \quad (12)$$

where E and ν are the Poisson ratio and Young's modulus of the coating respectively.

Table 1a. Strains calculated from thermal shrinkages $\epsilon_{\parallel}^{\text{th}}$ and strains $\epsilon_{\parallel}$ and stresses $\sigma_{\parallel}$ measured in TiC layers on Mo and W substrates

Layer	Substrate	Calculated $\epsilon_{\parallel}^{\text{th}}$ (%)	Measured $\epsilon_{\parallel}$ (%)	Measured $\sigma_{\parallel}$ (MPa)
TiC	Mo	0.16	0.15	820
TiC	W	0.23	0.21	1130
Error		± 0.03	± 0.006	± 40

Table 1b. Strains $\epsilon_{\parallel}$ and stresses $\sigma_{\parallel}$ measured for Mo and W substrates after deposition of TiC layers

Layer	Substrate	$\epsilon_{\parallel}$ (%)	$\sigma_{\parallel}$ (MPa)
TiC	Mo	-0.001	-2
TiC	W	-0.014	-57
Error		± 0.003	± 10

Measured and predicted strains/stresses* ($\epsilon_{\parallel}$, $\sigma_{\parallel}$) and ($\epsilon_{\parallel}^{\text{th}}$, $\sigma_{\parallel}^{\text{th}}$) in TiC coatings (thickness about 6 μm) obtained by CVD on Mo and W substrates (thickness 1.5–2 mm) are presented in Table 1 together with the corresponding measured strains/stresses in the substrates (Sloof *et al.* 1987*b*). It can be concluded that (i) the stress in the substrate (because of the limited penetration of the X-rays, substrate-stress values refer to a 5–10 μm thick region of the substrate adjacent to the coating) indeed is very small compared with the stress in the coating, and (ii) measured and predicted strains for the coating agree well.

(b) Inhomogeneous Chemical Composition and Stress

Owing to the presence of a concentration profile of component A in a direction perpendicular to the surface of the specimen, the lateral linear misfit can change as a function of depth z below the surface. Then a stress profile $\sigma_{\parallel}(z)$ can develop which

* Here $\epsilon_{\parallel}$, an average over all crystallites, is in principle *not* equal to the strain $\epsilon_{\psi=\pi/2}$ for those grains where the lattice planes utilised in the $\sin^2\psi$ analysis are perpendicular to the surface. The value for $\epsilon_{\parallel}$ is simply derived from the experimental value for $\sigma_{\parallel}$ by $\epsilon_{\parallel} = \sigma_{\parallel}(1-\nu)/E$.

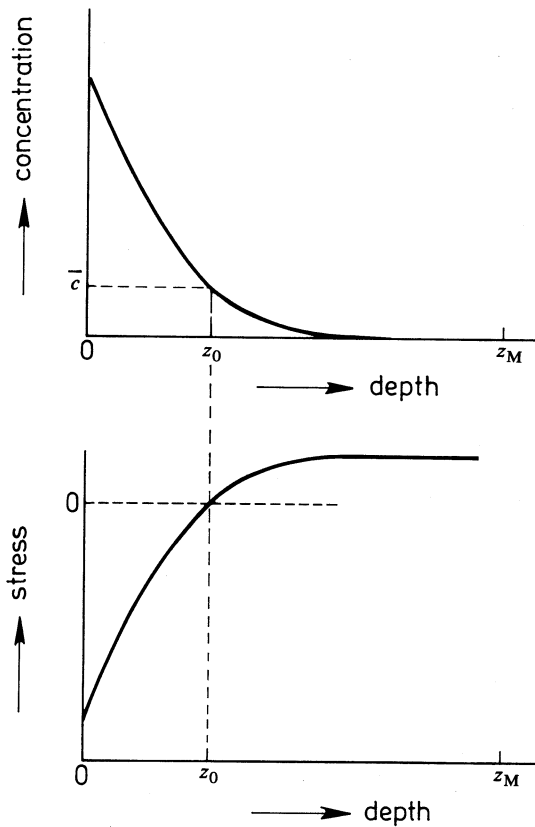


Fig. 4. Schematic drawing of concentration c and related stress σ as a function of depth in a plate-like specimen of thickness $2z_M$. For the case considered the lattice spacing increases with increasing concentration. Concentration and stress are symmetric with respect to the midplane at depth z_M . The depth z_0 indicates the neutral plane where the stress is zero. If the (stress-free) lattice parameter depends linearly on concentration, the concentration at z_0 is equal to the volume-averaged concentration $\bar{c}$.

is closely bound up with the concentration profile $c_A(z)$ (Fig. 4). Assuming complete elastic accommodation, straightforward modelling is possible here too (Mittermeijer 1984).

Consider again a specimen with plate geometry of infinitely large lateral dimensions containing a component A dissolved in a surface layer of the substrate. Then the 'compositional strain' $\epsilon_{\parallel}^c$ parallel to the surface reads

$$\epsilon_{\parallel}^c(z) = -\beta c_A(z), \quad (13)$$

where β is the fractional change of the lattice parameter per unit change of c_A (lattice-dilatation coefficient or Vegard's constant). If practically all strain is accommodated by the substrate-surface layer, it follows for the stress $\sigma_{\parallel}^c$ in the substrate-surface layer that

$$\sigma_{\parallel}^c(z) = \frac{E}{1-\nu} \epsilon_{\parallel}^c(z) = -\frac{\beta E}{1-\nu} c_A(z). \quad (14)$$

If the core of the specimen (free of A) is strained also (this can occur significantly for a relatively small core/surface-layer thickness ratio) and an analogous substrate-surface

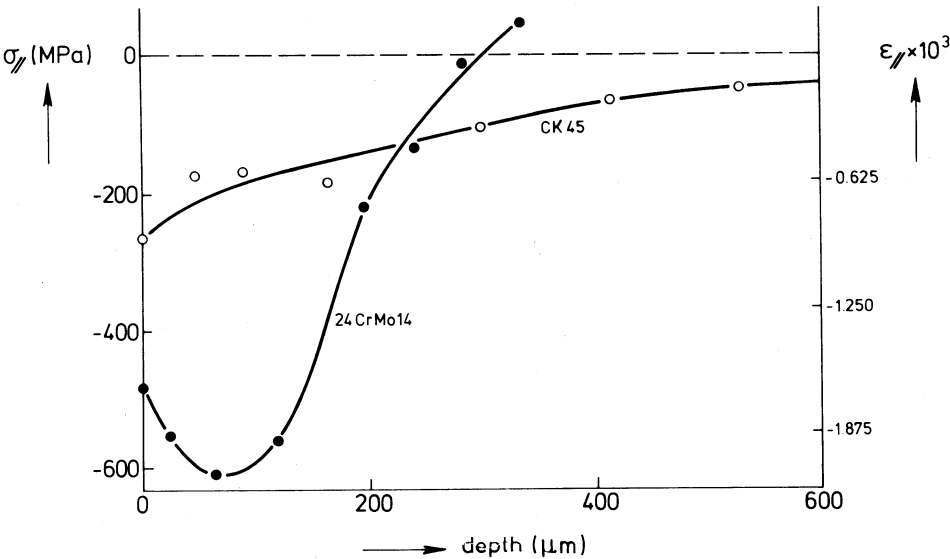


Fig. 5. Residual macrostress $\sigma_{\parallel}$ as a function of depth below the surface for specimens (thickness 8 mm) of steels Ck45 and 24CrMo13 (=En40B) nitrided in an ammonia atmosphere at 783 K for 20 h. Results were obtained from the Co K α {220} reflection of the α -iron phase. Correction for relaxation effects due to sublayer removal was made.

layer (containing A) occurs at the opposite side of the plate, the stress profile conforms to (Fig. 4; see also Fig. 5)

$$\sigma_{\parallel}^c(z) = \frac{\beta E}{1-\nu} \{ \bar{c}_A - c_A(z) \}, \tag{15}$$

where $\bar{c}_A$ denotes the average concentration of component A in the plate.

This model is of relevance for surface treatments such as carburising and nitriding where a substrate–surface layer develops enriched in carbon or nitrogen respectively. During cooling after nitriding of a carbon steel the nitrogen atoms can precipitate as iron nitrides, whereas in an alloy steel alloying-element nitrides can develop during nitriding. In both steels stress-depth profiles will be evoked; see Fig. 5 (Rozendaal and Mittemeijer 1983). These stress profiles in nitrided specimens of Ck45 (carbon steel) and of 24CrMo13 (=En40B or chromium-alloyed steel) were determined after successive sublayer removals, thereby performing a correction for relaxation effects due to sublayer removal. Obviously, owing to association between chromium and nitrogen atoms, the nitrogen uptake by the alloy steel is much larger than by the carbon steel. Consequently, larger compressive stresses but smaller nitrogen-penetration depths are observed for the alloy steel, as compared with the carbon steel. The decrease of compressive stress of the alloy steel towards the surface can be related to relaxation effects (see below).

(c) Stress Relaxation by Phase Transformations

If the absolute value of the stress measured is smaller than the absolute value predicted on the basis of elasticity theory, it can be concluded that part of the strain induced is accommodated plastically (only elastic strains are detected by X-ray diffraction analysis). Such strain accommodation is frequently denoted as ‘relaxation’.

Processes leading to relaxation can occur either in the surface layer, or in the substrate, or in both. Obviously, if locally the yield strength is surpassed, plastic deformation can be expected: a variety of corresponding relaxation mechanisms have been indicated in the literature, specifically for the surface layer, where normally the highest (predicted) absolute values for the stress occur (see the review by Murakami 1984).

The presence of microporosity (e.g. in CVD and PVD TiN coatings) and macroporosity (e.g. in iron nitride coatings) allows strain accommodation well before the internal stress would exceed the yield strength.

It is not well appreciated that phase transformations can provide an effective means for strain accommodation. Apart from the volume changes inherent in the phase transformation concerned, the high atomic mobility at moving interfaces, in association with the disruption and establishment of atomic bonds, can lead to adjustment of the atomic arrangement, in the ultimate case providing the equilibrium (i.e. stress-free) macroscopic configuration strived for. The phase transformation can occur in that part of the body which is the least stressed (e.g. the substrate in a coating/substrate assembly) but, if evoked, it brings about stress relaxation for the whole body, without any yield limit of the material being surpassed.

If a thin TiC coating is applied to a thick FeC substrate by CVD, it can be assumed that at the CVD temperature (e.g. 1273 K) no macrostresses result for coating and substrate. Stresses in coating and substrate develop during cooling from the deposition temperature to room temperature by the difference in thermal shrink between the TiC coating and the FeC substrate (see Section 3a).

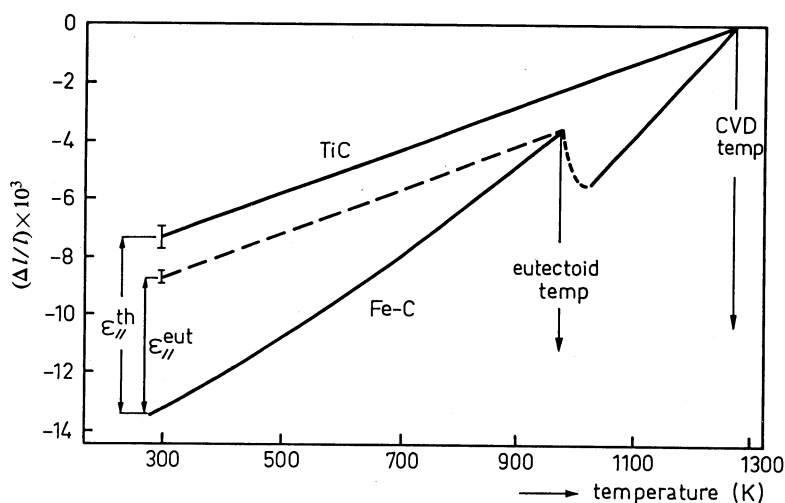


Fig. 6. Relative shrink $\Delta l/l$ of TiC and of an FeC alloy with 0.48 wt% C during cooling from the deposition temperature to room temperature. The expected strain $\epsilon_{||}^{th}$, and the strain $\epsilon_{||}^{eut}$ that would occur if the coating/substrate assembly was strain-free at the eutectoid temperature, are indicated.

At the deposition temperature FeC alloys containing less than about 1.5 wt% C are austenitic. On cooling, a 'normal' thermal shrink of the FeC alloy occurs until, at a certain temperature (depending on the carbon content of the alloy), in the hypo-eutectoid alloys ferrite and in the hypereutectoid alloys cementite starts to

form. On further cooling these processes continue until, at the eutectoid temperature, all remaining austenite transforms to pearlite. The total result of these phase transformations, which occur in a temperature range, is a volume increase of the alloy. During further cooling to room temperature a ‘normal’ thermal shrink occurs again. For the FeC alloys considered, cooling from the CVD temperature to room temperature yields a net shrink, while TiC experiences only a ‘normal’ thermal shrink (see also Fig. 6).

The difference in thermal shrink between coating and substrate will be predominantly assimilated by the coating. Then, according to the discussion above, a thermal strain value $\epsilon_{\parallel}^{\text{th}}$ (see Fig. 6) is predicted for the TiC coating. However, in all cases investigated until now experimental values for the strain are much smaller than the predicted ones (Sloof *et al.* 1987*a*).

Relaxation induced by (recovery) processes in the TiC coating is not likely since the yield strength and hardness of TiC are high at the temperatures occurring during the experiments. On the other hand the substrates have a low yield strength at the higher temperatures of the temperature range.

If it is assumed that the phase transformations in the FeC substrate during cooling lead to a full accommodation of the thermal strain then present, it follows that thermal strain builds up only below the temperature T_{eut} where the phase transformations have been completed. According to this picture a strain $\epsilon_{\parallel}^{\text{eut}}$ is predicted for the TiC coating, instead of $\epsilon_{\parallel}^{\text{th}}$ (see Fig. 6). Good agreement is found between the experimental strain $\epsilon_{\parallel}$ and $\epsilon_{\parallel}^{\text{eut}}$ (for a detailed discussion see Sloof *et al.* 1987*a*).

Table 2. Measured stress $\sigma_{\parallel}$, parallel to the surface, in an FeCr (3.61 wt% Cr) specimen (thickness 2 mm) after nitriding for 63 h in an atmospheric 10 vol% NH_3 /90 vol% H_2 gas mixture at 833 K

Depth (μm)	$\sigma_{\parallel}$ (MPa)
0	126
35	97
65	116
120	371
280	−411

An even more dramatic example of strain accommodation brought about by phase transformation is observed during the nitriding of FeCr and of FeCrC alloys (Hekker *et al.* 1985; Van Wiggeren *et al.* 1985). On nitriding a ferritic FeCr alloy a substrate–surface layer develops that, due to the precipitation of chromium nitrides, tends to expand. This expansion is counteracted by the unnitrided core. As a result a *compressive* stress parallel to the surface is expected for the substrate–surface layer (cf. Section 3*b*). This prediction is in strong contradiction with the experimental data shown in Table 2: near the surface a *tensile* stress is observed; only at larger depth is a compressive stress detected. The discrepancy between the naive expectation and the experimental outcome is ascribed to the phase transformation occurring in FeCr alloys on nitriding.

Initially *continuous* precipitation takes place of chromium nitrides with a submicroscopic size. Later, nucleating at grain boundaries, a *discontinuous*

precipitation reaction occurs, transforming the ferritic matrix containing coherent chromium-nitride particles into a lamellae-like structure of ferrite and coarse chromium nitride. This process starts near the surface and proceeds inwardly, following the nitriding front at some distance. This phase transformation can lead to (complete) accommodation of the then present strain. However, beneath the transformed layer the nitrided layer containing submicroscopic chromium nitrides continues to develop with an associated tendency to expand. In this way it can be understood that now stresses can develop of tensile nature in the earlier transformed layer and in the core, and of compressive nature in the layer containing submicroscopic nitrides (see Fig. 7 and Table 2).

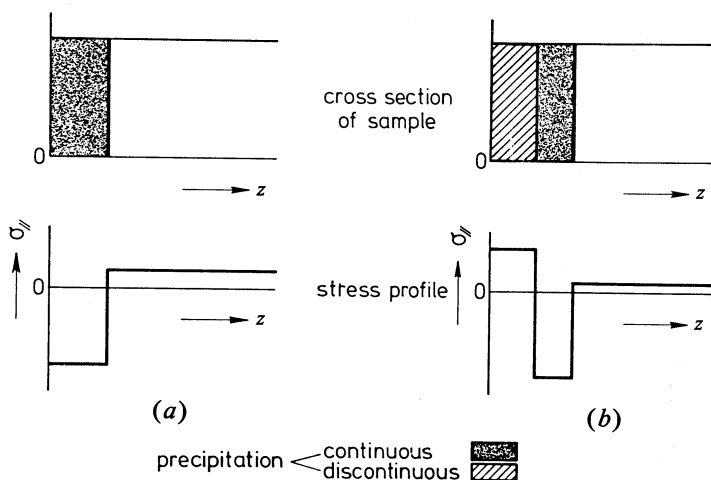


Fig. 7. Schematic presentation of the development of sample constitution and macrostress during nitriding FeCr alloys in the substrate-surface layers of the specimens. Parallel to the surface, (a) firstly a compressive stress develops in the surface layer when only submicroscopic, coherent nitrides occur (continuous precipitation); (b) later, relaxation phenomena due to the lamellar precipitation of ferrite and coarse chromium nitride (discontinuous precipitation) lead to a tensile stress in the surface layer.

It may be noted that during the phase transformations in both the (TiC covered) FeC substrate discussed above and the nitrided FeCr surface layer, lamellar structures develop, implying a multitude of interfaces being created.

4. Interdiffusion in Multilayers

At low temperatures the diffusivity will be relatively small. However, the diffusion-induced changes in X-ray diffraction patterns of systems with relatively small diffusion distances are significant and allow the study of processes rate-controlled by diffusion with diffusion coefficients as small as $10^{-27} \text{ m}^2 \text{ s}^{-1}$. For X-ray diffraction methods developed for analysis of interdiffusion in *bilayers* see Mittemeijer and Delhez (1980). Here attention is paid to diffusion-induced phenomena in *multilayers* composed of two components.

(a) *Diffusion in Amorphous Multilayers; Structural Relaxation*

If the kinematical diffraction theory can be applied and the effective interdiffusion coefficient D is constant, it follows that for the integrated intensity I of the m th order reflection of a multilayer with composition-modulation period Λ (see Section 2f and Fig. 1a)

$$\ln \frac{I_m(t)}{I_m(t=0)} = -\frac{8\pi^2}{\Lambda^2} m^2 D t, \quad (16)$$

where t indicates the time of diffusion. This equation has often been used for the analysis of interdiffusion in *crystalline* multilayers (e.g. Cook and Hilliard 1969).

In *amorphous* materials the diffusion coefficient is time dependent owing to structural relaxation. Usually the viscosity η of amorphous material increases linearly with the isothermal annealing time. Adopting the Stokes-Einstein relation η and D are related according to $\eta D = kT/6\pi r$, where T , k and r are the temperature, Boltzmann constant and average atomic radius respectively. The time dependence of the diffusion coefficient can then be given as

$$\frac{1}{D(t)} = \frac{1}{D(t=0)} + \alpha t, \quad (17)$$

where α is a temperature dependent constant. Taking into account this time dependence (16) should be replaced by (Sloof *et al.* 1986)

$$\begin{aligned} \ln \frac{I_m(t)}{I_m(t=0)} &= -\frac{8\pi^2}{\Lambda^2 \alpha} m^2 \ln\{1 + \alpha D(t=0)t\} \\ &= -\frac{8\pi^2}{\Lambda^2 \alpha} m^2 \ln \frac{D(t=0)}{D(t)}. \end{aligned} \quad (18)$$

To obtain α and $D(t=0)$, equation (18) can be fitted to the experimental data. If the term $\alpha D(t=0)t$ is large compared with 1, a plot of $\ln\{I_m(t)/I_m(t=0)\}$ versus $\ln t$ should result in a straight line.

The diffractogram obtained from an 'as sputtered' Mo/Si multilayer (200 nm thick, Mo/Si atomic ratio ≈ 0.6 and $\Lambda \approx 0.77$ nm) is shown in Fig. 8 (for details see Sloof *et al.* 1986). Only the first-order reflection ($m = 1$) is clearly detected; higher order reflections are not observed (see 2θ ranges a and b in Fig. 8). The absence of higher order reflections suggests that the concentration profile is of near-sinusoidal shape and/or that the composition-modulation period of the multilayer varies, leading to line broadening and a strong decrease of the peak intensity of reflections. A variation in the composition-modulation period may be understandable recognising that the Mo and Si sublayers have average thicknesses of only about one and two atomic diameters respectively: in view of the small average period, the occurring interfaces are relatively diffuse.

The part of the diffractogram (see Fig. 8) where reflections from crystalline Mo and Si or from silicide might occur only showed a broad intensity band peaking at about $42^\circ 2\theta$; this band is typical for the amorphous nature of the material. Except for the first-order reflection, the diffractogram did not change in the temperature range employed (480–573 K) for the annealing times applied. The application of the

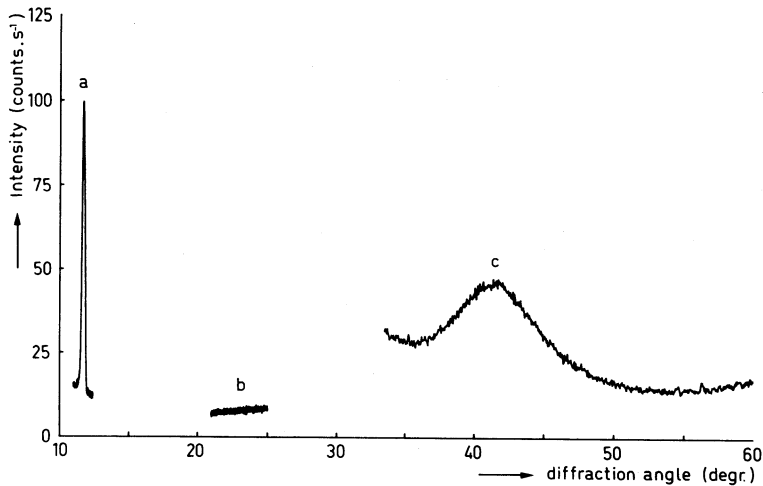


Fig. 8. Diffractogram (Cu K α radiation) of an 'as sputtered' Mo/Si multilayer specimen (Mo/Si atomic ratio is ≈ 0.6 , $\Lambda \approx 0.77$ nm and thickness is 200 nm): (a) 2θ range where the first-order ($m = 1$) multilayer reflection occurs; (b) 2θ range where the second-order ($m = 2$) reflection was expected; and (c) 2θ range where reflections of crystalline phases could be expected. The three parts were obtained with different counting time/step-size combinations.

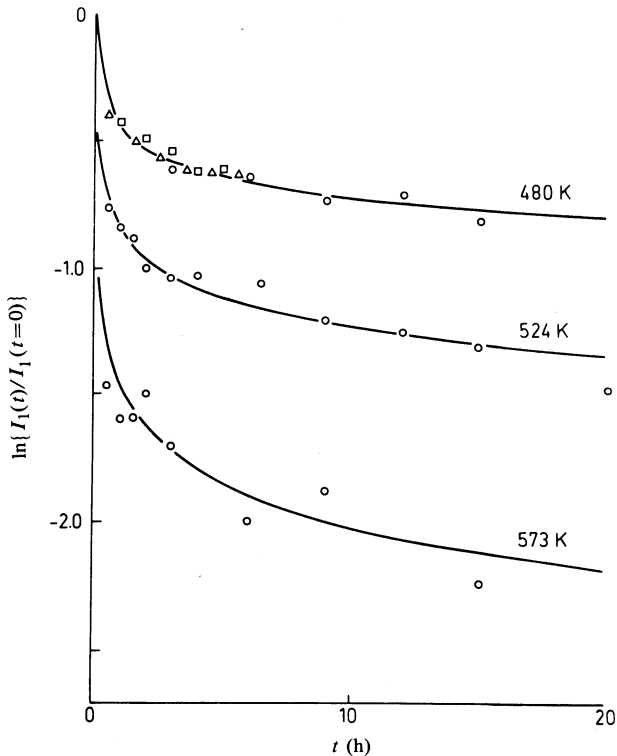


Fig. 9. Plot of $\ln\{I_m(t)/I_m(t=0)\}$ for $m = 1$ as a function of the annealing time t for Mo/Si multilayer specimens as described in Fig. 8. At each temperature one specimen was annealed cumulatively. At 480 K two additional specimens were annealed (triangles and squares).

kinematical diffraction theory is justified (cf. equation 16) considering the relatively low intensity of the multilayer reflection (see Fig. 8).

Separate specimens, but from one Si wafer, were used for the diffusion experiments at different temperatures. Fig. 9 shows $\ln\{I_m(t)/I_m(t=0)\}$ as a function of the annealing time for three annealing temperatures. The curves represent the results obtained by fitting (18) to the data. Good agreement with the measurements is achieved.

If the specimens are considered to be identical (=isoconfigurational) at $t = 0$, which is likely because they were obtained from the same Si wafer after a single sputter deposition, then it follows from the data obtained by fitting that (Fig. 9)

$$D(t=0) = 7.8 \times 10^{-16} \exp(-73 \text{ kJ mol}^{-1}/RT) \text{ (m}^2\text{s}^{-1}\text{)},$$

$$\alpha = 1.4 \times 10^{19} \exp(17 \text{ kJ mol}^{-1}/RT) \text{ (m}^{-2}\text{)}.$$

Interpretation of these data is speculative (for discussion of the above results see Sloof *et al.* 1986; Loopstra *et al.* 1987).

In amorphous materials structural relaxation implies a decrease of free volume usually designated as the free volume per atom v_f , expressed in atomic volume. In multilayer specimens the decrease of free volume Δv_f can be determined from the decrease of the composition-modulation period Λ derived from the position of the multilayer reflections. Because the multilayer is rigidly fixed to the substrate, a volume change is thought to be accommodated entirely by a change of thickness of the multilayer, and thus

$$\Delta v_f(t) = v_f(t=0) - v_f(t) = \frac{\Lambda(t=0) - \Lambda(t)}{\Lambda(t=0)}. \quad (19)$$

For the diffusion coefficient of metallic glasses one may write

$$D \propto \exp(-\gamma v^*/v_f), \quad (20)$$

where γv^* is a constant of the order 0.1 (Taub and Spaepen 1980). Then, a combination of (18)–(20) leads to (Loopstra *et al.* 1987)

$$\ln \frac{I_m(t)}{I_m(t=0)} = - \frac{8\pi^2}{\Lambda^2 \alpha} m^2 \frac{\gamma v^*}{v_f(t=0)} \frac{\Delta v_f(t)}{v_f(t=0) - \Delta v_f(t)}. \quad (21)$$

Now, in principle γv^* and $v_f(t=0)$ can be obtained by fitting (21) to the experimental data (intensity and position) of the diffraction maxima.

For a Mo/Si multilayer, annealed at 573 K in Ar such an evaluation is provided by Fig. 10. The error bars correspond to a $0.001^\circ 2\theta$ precision of the peak position determination. The curves represent (21) with $\gamma v^* = 0.1$, $\Lambda = 0.77 \text{ nm}$, $\alpha = 5 \times 10^{20} \text{ m}^{-2}$; the upper and lower curves are obtained with $v_f(t=0) = 2.2 \times 10^{-3}$ and 3.4×10^{-3} respectively. These values for $v_f(t=0)$ may be considered as limits for the actual value and can be compared with the free volume of about 1% reported for amorphous metals.

(b) Diffusion in Crystalline Multilayers; Amorphisation

An amorphous metallic alloy may be obtained by interdiffusion in an assembly of polycrystalline components of the individual elements. It has been proposed (Schwarz

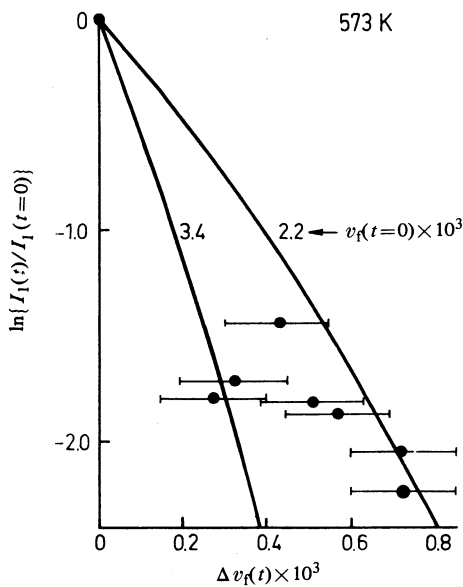


Fig. 10. Plot of $\ln\{I_m(t)/I_m(t=0)\}$ for $m = 1$ versus the decrease of free volume $\Delta v_f(t)$ for Mo/Si multilayer specimens as described in Fig. 8. The curves represent equation (21).

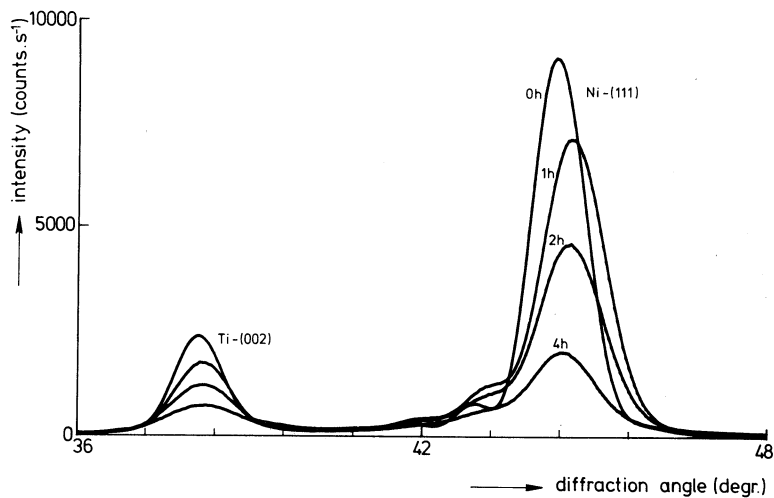


Fig. 11. High-angle part of the diffraction pattern of a Ni/Ti multilayer specimen (Ni/Ti atomic ratio is ≈ 1.7 , $\Lambda = 21.75$ nm and thickness is 400 nm) for several annealing times at 523 K (Cu $K\alpha$ radiation).

and Johnson 1983) that the formation of such a metastable amorphous phase may be preferred over the stable crystalline state if (i) a large negative enthalpy of mixing occurs in the liquid state, and (ii) one of the elements shows so-called anomalously fast diffusion in a crystal of the other element.

The Ni/Ti system is used here for illustration of amorphisation by diffusion in multilayers (for details see Jongste *et al.* 1988).

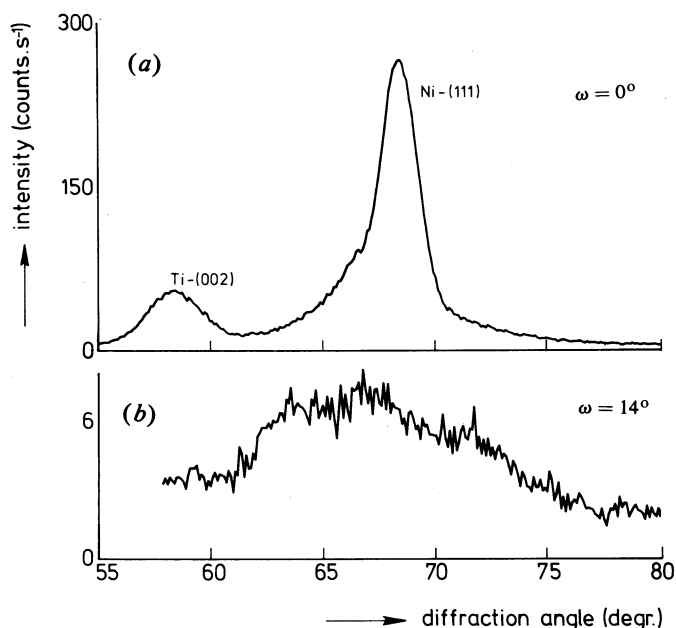


Fig. 12. High-angle part of the diffraction pattern of the Ni/Ti multilayer specimen described in Fig. 11 after annealing for 16 h at 523 K (Cr K α radiation): (a) tilting angle $\omega = 0^\circ$; (b) tilting angle $\omega = 14^\circ$, where the presence of the intensity band can be ascribed to the amorphous phase.

The high-angle part of the diffraction pattern of a Ni/Ti multilayer (20 Ni/Ti bilayers of approximately 20 nm each) is shown for progressive annealing times in Fig. 11: the integrated intensities of the Ni {111} and Ti {002} reflections decreased with annealing time at 523 K. Evidently one or more new phases were formed, since the Ni $\langle 111 \rangle$ and Ti $\langle 001 \rangle$ fibre textures remained extremely sharp and constant during the annealing. Strong indication for amorphisation was obtained by tilting the sample in the diffractometer (ω -tilting) and then performing a 2θ - θ scan to record the crystal reflections at various angles with the fibre axis. Already for moderate values of $\pm\omega$ the Bragg peaks vanished, but for the annealed samples an intensity band characteristic of an amorphous phase remained after tilting (Fig. 12).

The low-angle part of the diffraction pattern shows the multilayer reflections (Fig. 13). Bragg peaks up to the 16th order are visible. Using the modified Bragg law (8), the composition-modulation period Λ was determined as a function of annealing time. It decreased upon annealing (Fig. 14), thereby providing additional evidence for the formation of an amorphous phase, as amorphous $\text{Ni}_x\text{Ti}_{1-x}$ has a smaller molar volume than a mixture of crystalline Ni and Ti. Although the occurrence of solid-state amorphisation appears to be indicated by the above results, some observed diffraction effects are not understood and may be inconsistent with amorphisation (see Jongste *et al.* 1988).

As compared with the Mo/Si multilayers, the multilayer reflections are much more intense and the kinematical diffraction theory breaks down. Hence (16) cannot be applied.

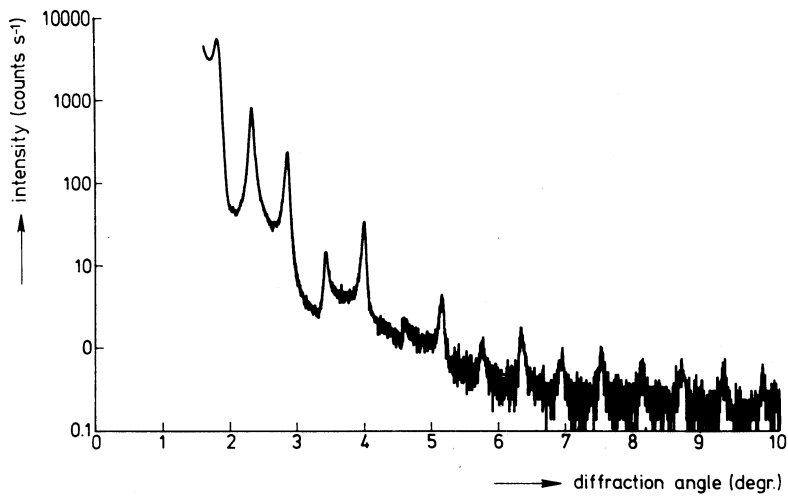


Fig. 13. Low-angle part of the diffraction pattern of the Ni/Ti multilayer specimen described in Fig. 11 showing the (00*m*) multilayer reflections up to the 16th order for the ‘as prepared’ condition (Cr Kα radiation and logarithmic intensity scale).

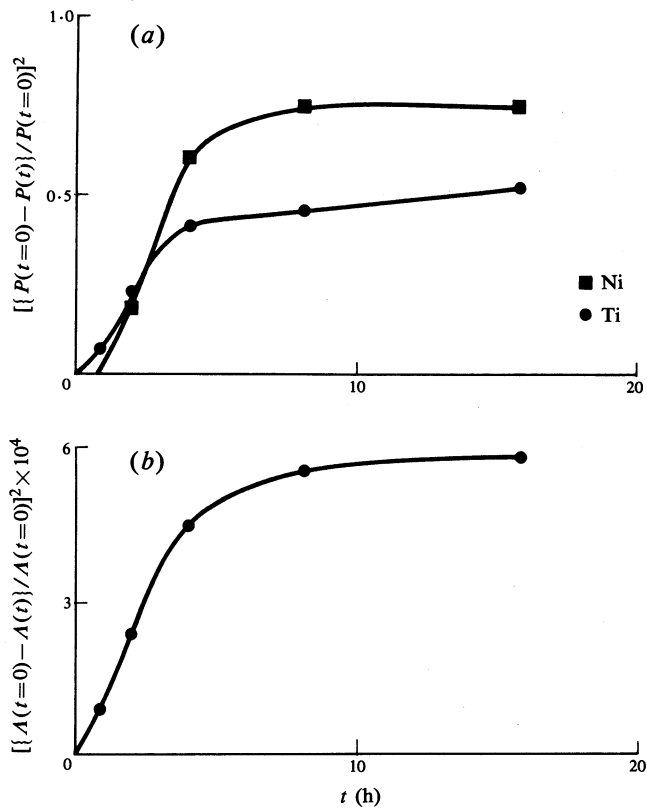


Fig. 14. (a) Squared relative changes of the integrated intensities P of the Ni {111} and Ti {002} reflections as a function of annealing time t at 523 K, for the Ni/Ti multilayer specimen described in Fig. 11. (b) Corresponding squared relative changes of the multilayer period Λ .

Since no significant change in texture was observed, the amounts of crystalline phases remaining after a certain time t are proportional to the integrated intensities of the crystal reflections. Fig. 14 shows $[\{P(t=0) - P(t)\}/P(t=0)]^2$, where P denotes the integrated intensity of the reflection considered, and $[\{\Lambda(t=0) - \Lambda(t)\}/\Lambda(t=0)]^2$ versus t . In the first part of the process the intensities and Λ show a parabolic dependence on t , which is typical for a diffusion controlled process. Applying a suitable model for the growth of a planar product layer, from the dependence of integrated intensity on annealing time, an interdiffusion coefficient was obtained. The preliminary results indicate that this diffusion coefficient is smaller than that corresponding to anomalously fast diffusion of Ni in α -Ti, but larger than those for self-diffusion of both components.

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