SURFACE PROPERTIES
AND ENGINEERING OF
COMPLEX INTERMETALLICS

edited by
Esther Belin-Ferré

CMA
complex metallic alloys
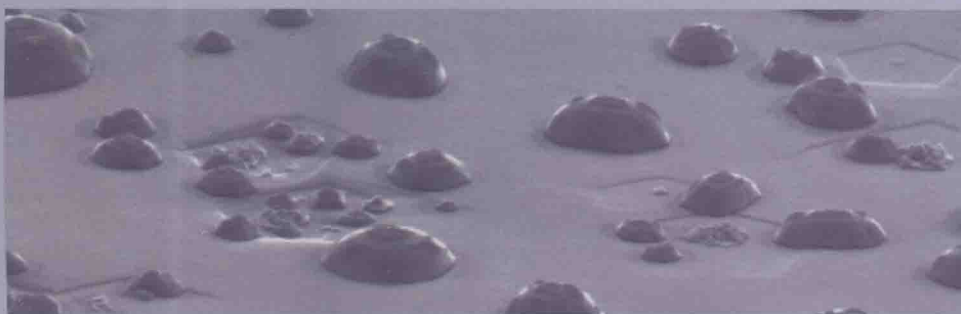**European Network of Excellence**

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Book Series on
Complex Metallic Alloys – Vol. 3

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Series on Complex Metallic Alloys

Series Editor: Jean Marie Dubois

FOREWORD

This is the third volume of a series of books issued from the lectures delivered at the Euro-School on Materials Science, organised yearly in Ljubljana, by the European Network of Excellence Complex Metallic Alloys (CMA) under contract NMP3-CT-2005-500145.

The third session of the CMA Euro-School, was mostly dedicated to surface properties and engineering of complex metallic alloys. Accordingly, this book collects contributions dedicated to preparation of thin films and their characterisation by various experimental techniques, their structural specificities as well as their physical, chemical and electronic properties, etc. The penult chapter reports about the catalytic potential carried by the surface of powdered complex systems whereas the last chapter presents a discussion about the validity of Hume-Rothery stabilisation mechanism applied to structurally complex alloys which complements the contents of volumes 1 and 2 of the series.

The European Commission is gratefully acknowledged for its financial support and warm thanks go to all the authors whose contributions have made possible the editing of the present volume.

Esther Belin-Ferré

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CHAPTER 1

PROPERTIES AND CHARACTERIZATION OF THIN FILMS

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An essential part of thin film science and technology is proper characterization of the film properties, which extends from scientific study to quality control in industry. Properties of thin films often differ considerably from properties of bulk materials of the same nominal composition. Another issue is the substrate influence on these properties, which is particularly important in characterization were we are usually looking for a result of thin film only. An overview of thin film properties is presented in this chapter and the techniques available to characterize them. Two groups of properties are discussed: structural properties (thickness, topography, crystal structure, microstructure, chemical composition), and mechanical properties (adhesion, stress, hardness).

1. Introduction

Materials science generally studies bulk solids. The sizes of a bulk object are roughly comparable in all three dimensions (length ≈ width ≈ height). If one of these dimensions is several orders of magnitude smaller than the remaining two (length ≈ width >> height), the laws of materials science do not change, of course. However, many effects negligible in bulk materials become important or even prevalent. When dealing with thin films we almost never analyze them as a separate object, such as a foil or membrane, but treat the whole object, substrate and thin film, as one system. Materials science of thin films therefore studies a simple composite: a three-dimensional substrate and (in first approximation) a

two-dimensional thin film on top of it.

This chapter will address three questions in each relevant property: (i) a brief overview on its basic physical background for bulk materials, (ii) what are the differences of this property in thin films compared to bulk materials, and (iii) how this property can be characterized.

The discussion of this chapter is limited to metallic and ceramic materials, with an emphasis on functional thin films in the micrometer range. Though most of the discussion is independent on the deposition type, it is primarily dedicated to films deposited by physical vapor deposition (PVD), because this technique is the most widely used for deposition of protective coatings. Specifically excluded are very thin films (a few monolayers thick) and very thick films (thickness in the 100 µm range), as well as soft materials (liquid crystals, biological materials).

Definition of basic terms is the next thing to be done at the beginning. Thin film is any type of material which covers the substrate having a thickness anywhere between monolayers up to hundreds of micrometers. Coating is usually regarded as a film which has a certain protective function to the film. The principle function of a hard coating is to act against wear. In this case the choice of thickness narrows to the order of magnitude of a micrometer, and the choice of materials reduces to those with high hardness and chemical stability. A film (or a coating) may be homogeneous in depth, may have a gradient of composition, or may consist of two or more layers. In schematic figures of this chapter, the substrate is always depicted in dark grey and the film in light grey.

1.1. *Types of thin films*

For protection of a substrate (Fig. 1a), deposition of a coating (Fig. 1b) is not the only option. Surface modification (Fig. 1c) is a group of methods which change the properties in the near-surface region of the substrate to enhance its resistance against wear, corrosion, etc. It may change its internal stress (e.g. sand blasting), crystal structure (e.g. surface heat treatment) or chemical composition (e.g. nitriding). The modified region typically does not have a clear boundary to the unaffected core part of the substrate; there is a rather gradual transition. A combination of the two, surface modification plus coating, is known as a duplex treatment

(Fig. 1d).
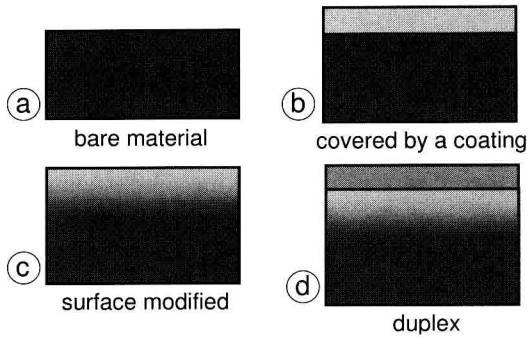
Fig. 1. Basic types of surface engineering techniques: (a) bare material, (b) covered by a coating, (c) surface modified, (d) surface modified and additionally covered by a coating (duplex).

We are talking about a *single layer film* (not to be confused with a monolayer), when its properties do not change with depth (Fig. 2a). In reality, no film is precisely homogeneous with depth as the deposition conditions at least slightly vary with time.
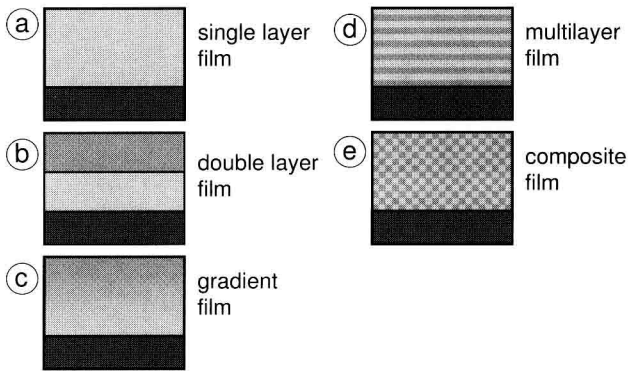
Fig. 2. Basic types of thin films: (a) single layer film, (b) double layer film, (c) gradient film, (d) multilayer film, (e) composite film.

A *double layer film* (Fig. 2b) is the simplest non homogeneous structure, where the deposition parameters are abruptly changed once during deposition. In most cases the two layers are distinguished by

composition (e.g. chromium above aluminum). However, the two layers can have identical composition, but different crystal structure, grain size or chemical state. If this change of deposition parameters is gradual, a *gradient film* forms (Fig. 2c). If the changes in deposition parameters (either discrete or gradual) are repeated several times, a *multilayer film* forms (Fig. 2d). The thickness of individual layers can be as low as a few nanometers; in this case, we are talking about nanolayers, or more broadly, nanostructured thin films. Most thin films are single-phase. When two different phases are present, more specifically, grains of phase A embedded in a matrix of phase B, such a structure is called a *composite film* (Fig. 2e).[1]

As noted in the previous paragraph, a thin film is never precisely homogeneous. Beyond minute gradients of composition, etc, there are typically two additional layers (Fig. 3): one at the interface (due to diffusion, ion bombardment or transient features at the deposition startup) and the other on top (in most cases a native oxide). These two layers are very thin (a few nanometers), but can have a sizable effect on properties like adhesion or friction.

toplayer (native oxide)
film (main part)
transition layer (inteface)
substrate
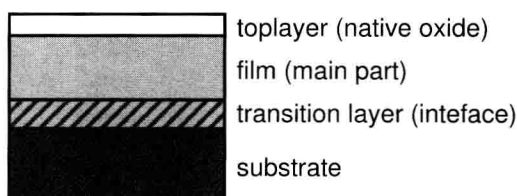
Fig. 3. Three layers of a typical thin film.

1.2. *Characterization of thin films*

A typical question might be: how much is the property A of a given thin film? Properties are quite different in regard to which part of a film they correspond. Surface tension is a property of the top-layer, adhesion is mainly a property of the film/substrate interface. In determination of film composition, both the interface and the top-layer are usually excluded. Often, the whole structure including the substrate contributes to a property, e.g. wear resistance.

Therefore we should consider the interaction volume that a characterization technique uses for evaluation. If the interaction volume is excessively large, we will measure primarily the property of the substrate. If it is very small, the result applies only to a small fraction of the film (e.g. one grain) and can in general not be extrapolated for the whole film. A typical example is Auger electron spectroscopy which has a penetration depth of a few nanometers; applying it to a typical surface will yield only the native oxide top layer. In this case, depth profiling is a necessary approach.

There are basically three ways to do depth profiling. One option is to focus, or at least adapt the probing beam or gauge to a desired depth (Fig. 4a). Examples include changing the impinging ion energy, changing the incident angle in X-ray diffraction, or changing the load in indentation experiments. No sample pretreatment is necessary, but the interpretation of the results can be quite complicated.
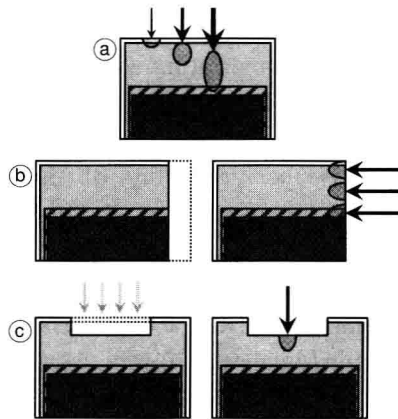
Fig. 4. Three ways of depth profiling: (a) tuning to a particular depth, (b) preparation of a cross-section (left), followed by a line scan (right), (c) periodic etching (left) and measurement (right).

The other option is to prepare a cross-section, either by grinding and polishing (Fig. 4b), or by braking the sample in two. Most techniques can be applied to characterize such a surface, but within the limits of lateral resolution. A helpful way of increasing the effective depth is to prepare a low-angle cross section. It should be kept in mind, that if the preparation

technique was conducted in ambient atmosphere, which is mostly the case, a thin oxide shale will form on the new surface, too.

Yet another option is, first to do selective etching and secondly perform analysis in the etched area Fig. 1.4c. If this procedure is repeated several times, a depth profile is obtained. This is a common way in several spectroscopic techniques, where etching is performed using a well-defined ion beam.

1.3. *Importance of thin film characterization*

A common question of a non specialist in thin films is: Why bother measuring all these properties, as they are all well known in the books? Two reasons speak against this. First, the properties of a thin film are often different from the property of a bulk material, even though the composition is nominally identical. Thin films deposited by PVD typically have lower grain size, a columnar microstructure, possible texture, high density of defects and large internal stress. In addition, metastable phases may form, supersaturated solid solutions, etc. In other deposition techniques, some of these effects may not be present, but a thin film will almost never be identical to a bulk.

The second reason is the variability of thin film properties in dependence of the deposition parameters. A set of thin films with an identical overall chemical composition may be a homogeneous polycrystalline compound film, a nanocomposite of two or more phases, an epitaxial, or an amorphous film. Characterization provides us the feedback, which parameters to choose to achieve a certain property.

This feedback is not straight-forward, though. *Deposition parameters* (e.g. substrate temperature, and technique-specific parameters, such as voltages) influence the *structural properties* of the film (microstructure, crystal structure, chemical composition). Structural properties in turn influence *macroscopic properties* (electrical conductivity, oxidation and corrosion resistance, hardness). The topmost level is the *application* of this film for a certain industrial or other use, where the lifetime, reproducibility or some other figure of merit is required. As an example, let us consider that in PVD deposition of TiN coating the bias voltage (deposition parameter) was set too high. The density of defects in the

film increased (structural property), which increased internal stress and reduced adhesion (macroscopic properties) and consequently reduced the tool lifetime (application). Nevertheless, it is pointless to oversimplify and say: too high bias voltage reduces the tool lifetime. All the intermediate steps are important too.

At the end, we should stress the limitations of thin film characterization, which will be important throughout the chapter. In bulk characterization the size of the interaction volume (shaded spots in Fig. 4) is not that important; in thin films, it should be in most cases below the film thickness. If this condition is not met, the ubiquitous substrate influence is included in our measurement which spoils the result. In such a low volume (radius of 1 µm and below), signal-to-noise ratio becomes smaller, and other effects – usually negligible in bulk measurements – become important, e.g. surface roughness.

2. Structural Properties

The inclusion of a certain property in "structural properties" is somehow arbitrary. The same holds for the term "mechanical properties" in the following subchapter. But this division is a convenient way to group similar properties. They are mainly microscopic properties in a way, which atoms are present, how they are bound and how the larger groups of atoms, i.e. grains are organized. The thickness would hardly be designated as a structural, nor mechanical property, but as it is the prime property of the thin films (thin means low thickness) it is explained at the beginning.

2.1. *Thickness*

Thickness is perhaps the first property encountered in thin films. It determines or at least influences most of the other properties. In certain applications (microelectronics, optics) the precision of thickness is critically important. In addition to the total thickness of the film, thickness of individual layers (if present) is also important. Thickness is determined by the deposition rate v and deposition time t:

$$d = vt \qquad (1)$$

Note, that the deposition rate is often not constant throughout the deposition. Even if we can maintain it more or less constant during peak power, this is not the case at the beginning and at the end of the deposition. In PVD techniques, in order to prevent arcing, power is often gradually increased towards peak value, which may take up to an hour. In this case, Eq. (1) is of limited value.

Besides changing in time, the deposition rate also considerably varies with substrate orientation. Though not an issue in deposition from solution, it is very important in PVD techniques. On the surface facing the deposition source, the growing film has a higher deposition rate, than on the surfaces pointing in other directions (Fig. 5a). The distance to the deposition source is also an important factor. The film will grow faster on substrates mounted closer to the deposition source than on those further away. In larger substrates this is exhibited as lateral inhomogeneity, which is a serious drawback in some applications (Fig. 5b). In holes, edges, ridges or other geometrical extremes, the thickness will inevitably vary greatly (Fig. 5c). The extent of these variations strongly depends on deposition type and its parameters. In order to deposit a film of equal thickness on complex-shape objects, the solution of choice is rotation of these objects. Though this generally averages all the variations in thickness, one has to be careful in multiple rotation modes where the deposition may still vary with direction.[2]
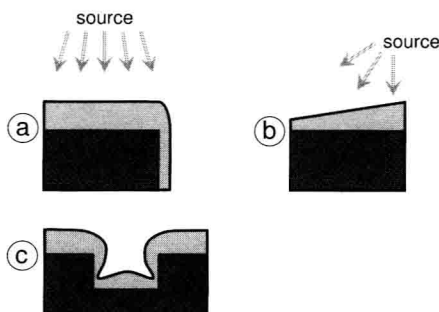

Fig. 5. Cases where thickness non-uniformity is expected: (a) surfaces pointing in different directions, (b) lateral non-uniformity due to increasing distance from the deposition source, (c) edges, holes and ridges.

When designing new thin-film structures, one often asks, what the

optimal thickness is. With an exception of applications, where this is dictated by the physics itself (e.g. quarter-wavelength in optics), the answer is a compromise. Thick films are preferred because of low substrate influence and later wear-out when exposed to the environment. The main disadvantages of thick films are a long deposition time (i.e. higher price) and often a high internal stress, which can lead to film cracking and delamination. Additional factors are connected to specific applications. At hard coatings, for example, the thickness ranges between 1 and 5 μm, depending on application.

There about twenty characterization techniques for evaluation of thin film thickness. We will concentrate on two of them which are very versatile and useful for laboratory work, have some words on two additional ones, and mention the remaining ones after that.

2.2. *Measurement of thickness*

A stylus profilometer is a device, which scans the surface using a sharp tip and records the displacement in z as a function of length x. The tip is usually a semicircular diamond, the measurement length can be up to several centimeters, while the vertical range is typically in the 100 μm range. An atomic force microscope (AFM, see next subchapter) can also be used for this purpose, however, due to its small scanning area and low maximum height it is seldom used (e.g. for very thin films).

In order to perform a thickness measurement by a profilometer, the sample has to be prepared in advance. Prior to the deposition, a mask is fixed on a part of the sample (typically a few millimeters wide). During deposition the mask prevents formation of the film in the protected area, and after removal of the mask, the boundary between the thin film and bare substrate becomes visible (Fig. 6a). When the stylus passes this boundary it records it as a step (Fig. 6b). The step height simply corresponds to the film thickness (Fig. 6c). An alternative way of step preparation is by selective removal of the film, usually by etching.

The advantages of this method is its easy operation, it is applicable to most material combinations and has a large range of step heights it can measure (tens of nanometers to tens of micrometers). Perhaps the biggest disadvantage is the fact that it needs pretreatment – positioning of a mask