Phase Analysis of Multilayered, Nanostructured Titanium-Base Alloys by Analytical Electron Microscopy

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Microstructure, chemical and phase composition of the hard layer formed on the Ti-6Al-4V alloy after duplex surface treatment were investigated by light microscopy (LM), X-ray diffraction (XRD) and analytical scanning, transmission and scanning transmission electron microscopy (SEM, TEM, STEM), electron diffraction and focused ion beam (FIB). Advanced electron microscopy techniques used for unambiguous identification of phases present in the surface multilayer are critically discussed. The relationship between multilayer micro/nanostructure containing several phases from the Ni-Ti-P-Al system and improved mechanical and tribological properties is established.

Keywords: Analytical transmission electron microscopy, scanning electron microscopy, scanning transmission electron microscopy, electron diffraction, titanium alloys, surface layers, nanostructure, characterisation, titanium-nickel-phosphorus coating, titanium nickel phosphorus phase

1. Introduction

Among extensive researches for developing hard coatings on titanium-base alloys since many years,¹⁴ nanostructured, multilayered/graded surface layers with enhanced mechanical and tribological properties aroused recently an increasing interest.⁵–⁷ In multi-component systems, such as titanium-base commercial alloys, it is not easy to predict the layer composition and microstructure that form during surface treatment, especially under non-equilibrium conditions (e.g. under plasma glow discharge). Therefore, characterization of surface layers by advanced analytical techniques, especially by cross-section transmission electron microscopy (TEM) is always mandatory.

Analytical electron microscopy is the only method to obtain simultaneously information about morphology, crystallography and chemical composition of the investigated phases with a spatial resolution at the micrometer level or even down to nano-scale. When the phases become very fine (a few to tens of nanometres or less), what is often a case, e.g. in nanomaterials, high-resolution transmission electron microscopy (HRTEM) is an attractive technique for characterization of nano-phases.

Crystallographic techniques—selected area electron diffraction (SAED), microdiffraction (µD) and high-resolution transmission electron microscopy (HRTEM) imaging—are the main tools for phase identification based on elastic electron scattering even in multiphase materials. Their first merit lies in the superposition of the information belonging to each phase when diffraction occurs from more than one phase, like in SAED for instance and to sort it, by dark-field imaging, for identifying which reflection belongs to a particular phase. The main limitation of diffraction methods is related to finite accuracy of experimental data what makes difficult to distinguishing isomorphic compounds or phases of very close crystal lattices, the need of a suitable description of the phase in a crystallographic database as long as identification is concerned and the relatively slow process of diffraction pattern analysis. An alternative method to nano-diffraction with very thin probe for nanophase is offered by recording crystallographic information by HRTEM followed by a Fourier transformation of nm-size HRTEM image area into diffractograms though it should never be forgotten that diffractograms are not diffraction patterns of the material itself but of its HRTEM image only.

Electron spectrometry methods (energy dispersive X-ray, EDS and electron energy loss, EELS) based on inelastic interaction are straightforward methods to measure a chemical composition of the phase under electron probe. However the concentration measured is a mean value for all atoms of the excited volume and if the probe diameter can be reduced to nanometres or even Angstroms, the averaging through the sample thickness cannot be avoided nor deconvoluted. Additionally these methods may lead to errors resulting from X-ray absorption, spurious signal due to electron scattering out of the probe and electron channelling. A review on the nano-phase identification techniques, their merit and limitation is given in Ref. ⁸).

The present study is related to the development of functionally graded titanium-base alloys with improved hardness and wear properties.⁴,⁵ The paper is focused on a detailed characterisation of the micro/nanostructure (especially phase identification) of the surface multilayers formed on the Ti-6Al-4V alloy during duplex surface treatment under glow discharge. Unambiguous identification of phases present in the multiphase multilayers, by a combination of advanced electron microscopy techniques described above, is critically discussed.

2. Experimental

The investigations were performed on the commercial α + β Ti-6Al-4V alloy annealed at 700°C for 2h. The as
delivered alloy was subjected to a duplex surface treatment consisting in a chemical electroless co-deposition of nickel and phosphorus followed by annealing at 800 °C/4 h under glow discharge.3)

The micro/nanostructure analyses were carried out by several microscopy methods, light microscopy (LM), scanning (SEM), analytical/high resolution transmission electron microscopy (TEM/HRTEM) and X-ray diffraction (XRD). Electron microscopy investigations were performed on plan-view and cross-section thin foils, prepared by conventional ion milling and by focused ion beam (FIB) milling, with JEOL JEM-2010 ARP, PHILIPS CM20T and PHILIPS CM300 UT/FEG electron microscopes equipped with STEM and energy dispersive X-ray spectrometer (EDS). Phase identification was done by electron diffraction (SAED, nanodiffraction), STEM-EDS and HRTEM. The diffraction patterns and HRTEM images were interpreted with the JEMS software.10) LM and TEM image analyses were performed using AnalySIS programme.11)

3. Results and Discussion

LM investigations show that the surface of the treated alloy is modified to a depth of some 130–200 µm (Fig. 1). A thin surface layer (10–20 µm) lies on an intermediate layer which contains much larger grains of α phase penetrating the α + β fine microstructure. It seems enriched by Ni, at least 6 at% Ni were found at 3 µm below the thin surface layer.

Further analytical TEM investigations show that the microstructure of the outer surface layer is much more complex than expected from LM observations. This multilayered coating, 10–20 µm thick, may be divided into five main sublayers labelled L1 to L5. Figure 2 shows a TEM bright-field image of the outermost layer L1-L4 sublayers (thin foil prepared by “classical” ion-milled cross-sectioning). Further observation in STEM annular dark-field (STEM-ADF) has the advantage because of its strong Z-contrast to better reveal the different kind of phases although on that sample changes in thickness partly hide it.

In the first part of this study, TEM was performed on “classical” cross sections prepared by gluing face to face the treated surfaces of two pieces and then thinning a slice by argon ion milling to electron transparency. Due to the different rates of sputtering of each material, the thickness increases quite rapidly from the glue to the substrate. Therefore EDS microanalysis are strongly biased by a spurious contribution of the substrate, mainly increasing the apparent Ti, Al and V content in the grain under investigation, and the apparent composition are not relevant of the observed phases. Figure 3 shows how stray X-ray photons are produced by electrons scattered by the TEM sample towards the microscope polepieces or electrons trapped in the magnetic field of the objective lens eventually hit the bulk part of the foil within the acceptance angle of the EDS collimator. This spurious signal precludes from any quantitative analysis or phase identification by EDS. Therefore, the EDS performed on “classical” thin foils was considered as a qualitative tool only.

STEM-ADF investigations of the surface layer with the EDS microanalysis show that phases containing Ti, Ni, P, Al, V and O should be considered for diffraction patterns interpretation. It lead to define a first set of possible phases based on these elements and the phases referenced in the ICCD (PDF-4) and ICSD (FIZ/NIST) database of crystal structures. Those with V were removed to make the set lighter, though it contains still some 40 phases. Based on this set, systematic phase identification by electron diffraction and HRTEM using the diffraction pattern indexation routines of JEMS was performed.

The results of phase identification, based on their diffrac-
tion patterns, in particular sublayers are summarised in Table 1.

The outmost sublayer L1 has a columnar microstructure. Its diffraction pattern fits the NiTi\textsubscript{2} crystallographic lattice. But it contains some 10\% at Al, thus it might be necessary to extend the set of possible phases to account for more Al-rich phases or to consider some substitution of Ti by Al. Both L2 and L3 sublayers exhibit equiaxed nanocrystallites. In the sublayer L2, the NiTi\textsubscript{2} and Ni\textsubscript{3}Ti phases and some TiO are present, while in the sublayer L3, the NiTi\textsubscript{2} and Ti\textsubscript{3}P phases are found. The L4 consists of larger grains of Ni\textsubscript{3}Ti, Ti\textsubscript{3}P (or Ti\textsubscript{5}P\textsubscript{3}) and AlNi\textsubscript{2}Ti phases. Moreover, the presence of some minor phases cannot be excluded. Finally the L5 sublayer contains mainly NiTi\textsubscript{2} with the exception of a discontinuous layer of Ti\textsubscript{3}P nanocrystals. EDS analysis shows that V (1–4 at\%) is also present, although no specific V-rich compounds were searched for up to now.

In a second part of the study, samples were prepared by Focused Ion Beam (FIB) cutting and milling. Prior to FIB processing a SEM observation of the sample treated surface (Fig. 4) revealed the presence of hillocks and nanoparticles adhering to the surface. EDS microanalysis failed to reveal local surface composition changes despite of the use of the lowest accelerating voltage compatible with the elements sought for to keep the primary electrons interaction volume and penetration depth as small as possible. Figure 5 shows an image of the layers under the surface during the FIB cutting (FIB/SEM, secondary electrons contrast). The L1 layer has clearly a non uniform thickness and is nearly absent on most of the thinned area, but under the hillocks. Moreover the sublayer L4 looks more complex than thought and must be subdivided into L4a, b, c, d.

The uniform thickness of TEM thin foils prepared by the lift-off technique offers the advantage over a conventional ion-milled cross-section of a better readability of individual grains. In particular in annular dark field scanning transmission microscopy (ADF-STEM), the chemical Z-contrast makes the different phases (labelled 1–8 on Fig. 6 and in Table 2) easily distinguishable when the grains are large enough to occupy the overall thickness of the thin foil. Moreover, the absence of thick substrate parts makes quantitative EDS analysis possible and, as long as no allotropic forms are present, phase identification becomes straightforward from simple chemical consideration. The
main drawback of FIB lift-off preparation remains the limited depth that can be reached below the surface, about 6 µm, that would require several lamellas sampled at different depth to cover the overall surface layer structure down to some 15 µm or even 200 µm if the full intermediate layer seen in LM would be investigated.

Table 3 summarizes the phases found from EDS spectra acquired in less than one minute each, i.e. with a statistical relevancy of compositions close to 5%. Phases Ti₃P, Ti₃P, Ni₃Ti and AlNi₃Ti were unambiguously observed within the sublayer L₄ (Fig. 6 and Table 2) and partial substitution of Ti by Al in several phases became obvious what electron diffraction failed to reveal.

But the more striking is the presence of a phase with a composition close to TiNiP that constitutes most of the L₄a sublayer and about 50% of the L₄b one. This phase is absent from the ICCD (PDF-4) and ICSD databases and was long thought to be unknown. Eventually it appeared that a phase Ti₃-P, Ti₃-P, Ni₃Ti and AlNi₃Ti were unambiguously observed within the sublayer L₄ (Fig. 6 and Table 2) and partial substitution of Ti by Al in several phases became obvious what electron diffraction failed to reveal.

(2) Most phases are directly and easily revealed by STEM dark-field imaging (strong chemical Z-contrast) on constant thickness thin foils prepared by FIB. The use of the FIB lift-off technique (no remaining thick part of the substrate) allows a direct identification of phases from the compositions measured on EDS spectra.

(3) Our diffraction study on the TiNiP phase, absent in ICCD (PDF-4) and ICSD databases, formed during duplex surface treatment shows that this phase has an orthorhombic structure close to that proposed by Lomnitskaya.

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