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Optimization of pulsed laser atom probe (PLAP) for the analysis of nanocomposite Ti–Si–N films

Fengzai Tang [a], Baptiste Gault [b], Simon P. Ringer [a], Julie M. Cairney [a,*]

[a] The Australian Key Centre for Microscopy and Microanalysis, The University of Sydney, Sydney, NSW 2006, Australia
[b] Department of Materials, University of Oxford, Parks Road, Oxford OX13PH, UK

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ABSTRACT

Laser-assisted atom probe tomography was used to investigate the nanostructure and composition of high-performance, ultra-hard Ti–Si–N nanocomposite films. However, the quality of data is heavily dependent on analysis conditions. In order to obtain reliable data from these, and other 'less conducting' specimens, the analysis parameter space was thoroughly investigated to optimize the mass resolution and hit multiplicity obtained in atom probe tomography. Geometric factors including tip radius and shank angle were found to play a significant role in mass resolution but had no apparent effect on the number of multiple hits observed. Increased laser energy led to a gradual increase in the number of single hits, but a modest improvement in mass resolution. The influence of other instrumental factors including detection rate and base temperature was investigated separately. Preliminary PLAP results are presented, and correlated with TEM analysis of the microstructure of the film.

1. Introduction

In the last decades there has been great interest in nanocomposite coatings with very high hardness due to promising applications in the machining industry. Binary nanocomposites of titanium silicon nitride, believed to consist of nanocrystalline TiN and amorphous Si_3N_4 [1] (hereafter designated nc-TiN/a-Si_3N_4), are typical of such new-generation coatings. Vickers hardness of up to ~40–50 GPa can be obtained, which is much higher than that of nanocrystalline TiN coating without Si [2]. The hardness of the coatings increases as Si is added to TiN up to a critical point, after which it drops back down. This effect is thought to be the result of the microstructure, and the structure of nc-TiN/a-Si_3N_4 with the largest hardness corresponding to a model in which the nano-sized TiN grains are encapsulated by an amorphous Si_3N_4 monolayer (~0.4 nm [3]) approaching the percolation threshold. A variety of analyses such as SEM, TEM and XPS have suggested that such a microstructure exists, however no direct evidence of the grain boundary decorated with this Si_3N_4 layer has been provided till date [1,2]. Atom probe is a technique highly suited to the measurement of compositional fluctuations over small size scales and may be able to, for the first time, provide evidence of the real microstructure of such specimens. However, in order to achieve this, high-quality atom probe data will be required.

Atom probe tomography (APT) [4–7] can provide unique three-dimensional information with near-atomic-scale resolution and a high sensitivity in compositional analysis. In 2005, Veprek et al. [2] attempted to investigate nanocomposite film by atom probe tomography, and found that mechanical instability of the specimen was an obstacle to overcome for analysis. Skogsmo et al. [8] studied a TiN coating in 1986 using atom probe field ion microscopy, in which samples were prepared by directly coating TiN film onto a pre-sharpened tip. Using the same specimen preparation method Ai et al. [9] studied TiN films using a custom-made pulsed-laser atom-probe FIM, and through depth profiling of very thin coated film TiO impurities were found to be concentrated at both the interface and the near top of the film surface.

The replacement of voltage pulsing by a pulsed laser (i.e. PLAP) in atom probe, first initiated by Kellogg and Tsong [10] in 1980, has been recently further studied both theoretically and practically [11–13] and the application of atom probe has been greatly widened [14–16]. Indeed, high voltage (HV) pulsed APT is mainly used to analyze samples with conductivities larger than $\sim 10^{-2}\,\Omega^{-1}\,cm^{-1}$ [14], and is not suitable to analyze less conductive non-metallic materials due to the improper transmission of pulsed voltage down to the tip apex. The use of pulsed laser sources enables this limitation to be overcome.

Concomitantly to the development of a new generation of pulsed laser atom probes, the last decade has seen another

* Corresponding author.
E-mail address: julie.cairney@sydney.edu.au (J.M. Cairney).

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significant contribution to the progress of atom probe techniques, the implementation of dual beam techniques, i.e. focused ion beam (FIB) and scanning electron microscopy (SEM), for specimen preparation [17]. This method has widened the application of APT to materials with a variety of geometries such as films and particles and has allowed the preparation of samples from site-specific regions [18].

In the present study, we have investigated the analysis performance of FIB-prepared samples of TiSiN films coated on steel substrates with respect to multiple events and mass resolution to provide optimum analysis conditions for reliable atom probe microscopy and microanalysis. The event multiplicity refers to the average number of ions detected that were generated by a single pulse. Multiple events and mass resolution are the two parameters that deeply affect the detectability, sensitivity and the accuracy of compositional measurements in atom probe tomography. It is expected that these conditions may also be used as a guide for other specimens investigated using PLAP. We will report preliminary results obtained from PLAP and TEM, but detailed structural and compositional analyses will be presented separately in another paper on the microstructure of TiSiN.

2. Experimental

2.1. Preparation and initial characterisation of nanocomposite Ti–Si–N film

Nanocomposite Ti–Si–N films were deposited onto steel substrates using a hybrid cathodic arc evaporation and chemical vapor deposition system, where a high purity titanium (99.95%) source is used to produce Ti atoms and silicon is generated from a liquid precursor of tetramethylsilane (TMS, Aldrich, 99.9% purity). Further details of the deposition process are provided elsewhere [19]. Two samples were produced with nominal compositions of ~2at% Si (sample 1) and ~8at% Si (sample 2). Cross-sectional TEM films were prepared by tripod polishing and thinned using Ar source milling. The morphology of the film was then analyzed by high resolution TEM (JEOL 3000F).

2.2. APT tip preparation and TEM examination

Needle-shaped APT tips for laser atom probe were prepared using a FIB-based 'cut-out method' previously reported by Saxey et al. [20]. Two kinds of dual beam instruments, a FEI Quanta 200 3D and a FEI Helios NanoLab 600 were used to mill tips. The regions of interest of specimen were firstly Pt coated in-situ and then milled using annular ring patterns from the top surface of deposited film towards the substrate. Initial cuts were made at 30 kV and final milling/cleaning made at reduced accelerating voltages down to 2 kV. SEM imaging together with energy dispersive spectroscopy (EDS) analyses were used to closely monitor the position of the film. Most APT tips prepared were examined by TEM (Philips CM12, 120 kV) either before or after atom probe analysis using an in-house designed holder. Some tips were examined at tilts from -20° to 20° in order to estimate the radius of curvature and shank angle of the tip, providing valuable information for 3D reconstruction of the data.

2.3. Pulsed laser atom probe (PLAP) analysis

A pulsed laser atom probe LEAP® (Imago Scientific 3000X Si) with a wide-field-view detector was used in this study. The laser source has a wavelength 532 nm with a pulse duration ~10 ps and a spot diameter ~15 μm. Experiments were carried out at a constant flight length of 90 mm, with a laser pulse frequency of 250 kHz, and the vacuum state was below $\sim 10^{-10}$ Torr in the analysis chamber. The laser was aligned to maximize the detection rate. The data obtained at different settings were studied in terms of both the mass resolution and the proportion of single hits. The voltage was varied during collection in each run, unless specifically stated, in order to maintain the detection rate. Reconstruction was carried out using the commercial software IVAS™ (Imago Scientific). The experiments conducted are listed in Table 1.

Firstly the effect of temperature (# 1) and detection rate (# 2) on single hits and mass resolution were separately evaluated. A single APT tip made from sample 2 (~8at% Si), was probed at temperatures of 30, 40, 50 and 60 K with a constant laser energy of 1.00 nJ and a detection rate of 2.5×10^{-3}at% per pulse, followed by repeated runs at 40 and 30 K. Around 1 M hits were collected in the first run at 30 K and ~0.5 M were collected in each subsequent run. Different detection rates of 5.0×10^{-3}, 7.5×10^{-3}, and 1.0×10^{-2} per pulse in average were then used at a constant laser energy (1.00 nJ) and temperature (30 K), followed by two repeated runs at detection rates of 5.0×10^{-3} and 2.5×10^{-3}. Around 1 M hits were collected in each run.

The influence of the laser energy was investigated at a constant base temperature of 50 K and a detection rate of 2.5×10^{-3} per pulse on average. In a first set of experiments (# 3), laser energies of 0.25–1.25 nJ per pulse were used with a step of 0.25 nJ, and the voltage was adjusted to keep the detection rate constant. The laser energies of 0.25 and 0.50 nJ were then repeated so as to consider the influence of tip radius, followed by a final step of 1.50 nJ. All runs were performed on a single tip from sample 1 (~2 at% Si). About 1 M (million) total hits were collected from each run. A second test up to 1.00 nJ was also conducted on a separate tip from the same sample. In a second set of experiments (# 4), once a detection rate of 2.5×10^{-3} per pulse in average was achieved, the corresponding voltage was kept constant while leaving detection rate dropping down automatically until ~0.5 M total hits in each run were collected. Under these conditions, experiments were conducted at laser energies from 0.25 to 1.50 nJ.

A number of APT tips from both samples were analyzed and larger datasets of up to 11 M total hits were collected in order to study the influence of the specimen geometry (end radius and shank angle) on the mass resolution and event multiplicity. All runs were conducted at the same laser energy (1.00 nJ), but either at a detection rate of 2.0×10^{-3} per pulse with a base temperature 30 K or at a detection rate of 2.5×10^{-3} per pulse with 50 K. For the end radius, it was done by analyzing a number of sequentially collected datasets from both samples conducted at 30 K, each with ~1 M hits.

3. Results

3.1. APT tip before and after LEAP examination

Fig. 1(a) is a SEM image of a FIB-prepared APT tip prior to LEAP examination. Fig. 1(b) is a TEM dark field image of such a tip, prepared from sample 2, in which some of the nano-scale grains in the nanocomposite Ti–Si–N film are highlighted. Inset is an electron diffraction pattern from this tip, confirming the cubic fcc TiN structure, and revealing no strong texture. A long TEM examination has lead to build-up of carbon on the surface that is visible in this figure as a bright region on the sidewalls of the tip. No obvious effect on APT analysis was noted. Fig. 1(c) shows a tip after the collection of ~7 M hits, with a rounded surface at the tip apex. In this figure the arrow indicates the position of the