Atom Probe Tomography - A Cornerstone in Advanced Materials Characterisation

KID: 20250115

There is an increasing number of advanced materials that are tailored at the nanoscale for specific applications, and therefore, it is imperative to understand the relationship between the atom-scale structure of a material system and its properties or performance. Advanced microscopy techniques play a crucial role in the design of these materials and devices. In the past few decades, electron microscopy has made great strides in this direction, such as the continued development of electron tomography and the advent of sensitive elements detection systems [1]. Further, aberration-corrected transmission electron microscopy can provide structural and compositional information in two dimensions with unprecedented atomic resolution [2].

Atom probe tomography (APT) is an effective technique for materials characterization, serving as a complementary tool to electron microscopy while offering distinct microstructural insights. This technique offers both 3-D imaging capability and atomic-scale chemical composition measurements, which make it unique among material analysis techniques. Due to its outstanding spatial resolution ($(\Delta x \approx \Delta y \approx 0.3\text{-}0.5$ nm and $\Delta z \approx 0.1\text{-}0.3$ nm) and detection sensitivity element concentrations down to a few ppm can be detected irrespective of elemental mass. The atom probe consists of a time-of-flight mass spectrometer and a point projection microscope capable of imaging at the atomic level.

Fundamentals of atom probe tomography:

The atom probe tomography (APT) technique evolved from field ion microscopy, which was first used to image individual atoms in the 1950s [3]. APT uses the intense electric field, typically on the order of tens of Vnm^{-1}, causing the constituent atoms of a material to be progressively repelled from the surface and ionized, either singly or multiply, through the field evaporation mechanism. The electric field necessary to produce the evaporation of an atom can be called the evaporation field, and it is specific to each element and phase in the material [4]. Conventionally, field evaporation is triggered by DC high voltage, which generates approximately 50-80% of the evaporation field. An electric field ($\sim 10^{10}$ V/m) is created at the apex of a sharp specimen (<100 nm radius) held at cryogenic temperatures when a high voltage (~10 kV) is applied. The application of voltage between the specimen and a local electrode facilitates the selective application of the field to a single specimen. By applying either voltage or laser pulses, surface atoms are field ionised and evaporated, atom by atom, layer by layer, towards a position-sensitive detector, where detector collects the ions and records their impact location. The utilization of voltage-pulsing enables the measurement of the time-of-flight for each individually detected ion. Time-of-flight directly correlates to mass-to-charge ratio, thus enabling elemental identification of individual ions.

The evaporation sequence provides information on the depth of the atoms at the specimen's apex, while the hit location on the detector determines their original position on the specimen. Using an inverse projection reconstruction algorithm and the sequence of detected events, the evaporated volume is then reconstructed in three dimensions. Typically, the tomographic data set comprises the spatial coordinates and elemental identities of several millions of atoms with nearly atomic precision, typically spanning tens to hundreds of nanometres in depth. The APT technique has become an indispensable tool in the study of metallic materials, advanced ceramics, semiconductors, biomaterials, and geosciences.

LEAP 6000 XR at the SATHI-CISCoM at IIT Hyderabad:

At SATHI-CISCoM, the atom probe lab houses the state-of-the-art LEAP (Cameca, LEAP 6000 XR) along with a focused ion beam (JEOL, JIB 4700F) for atom probe specimen preparation. The SATHI Centre for In-Situ and Correlative Microscopy (SATHI-CISCoM) at IIT Hyderabad is set up by a consortium of 18 partner institutes and with the support of DST through the SATHI program.

SATHI-CISCoM is the first centre in the country to enable real-time characterisation across multiple length scales for fundamental and industrial R&D purposes. Through this initiative, scientists from a variety of scientific disciplines, including metallurgy, materials sciences, physical sciences, and chemistry, will come together to address common scientific goals that can only be addressed through the use of sophisticated microscopy techniques. Designated students/scientists/technical staff of each partner institution have been trained on the operation of the LEAP, data acquisition and data analysis.

> *"Atom probe tomography (APT) is an effective technique for materials characterization, serving as a complementary tool to electron microscopy while offering distinct microstructural insights."*

Figure 1: Photographs of LEAP 6000 XR and demonstration to delegates at the SATHI-CISCoM, IIT Hyderabad.

Characterisation of precipitates and ordered phases in a high entropy super alloy:

The atom probe characterisation of $Ni_{39.7}Co_{32.2}Cr_{16.1}Al_6Ti_6$ medium entropy alloy was carried out using LEAP 6000 XR. APT studies were conducted using a laser with a wavelength of 257.5 nm (UV). To mitigate preferential evaporation of different elements and errors resulting from thermal vibrations, the specimen temperature was maintained at 60 K. Pulsed laser energy, pulse frequency, and data collection rate were 40 pJ, 200 kHz, and 0.5% per field evaporation pulse, respectively [5].

The partitioning coefficient ($K_i=C_i^{\gamma'}/C_i^{\gamma}$) characterises the preferential partition of element i between the γ and γ´ phases, where $C_i^{\gamma'}$and C_i^{γ} represent the elemental concentrations in the γ´ and γ phases, respectively. Elements with K_i >1 preferentially partition to the γ´ phase, while those with K_i <1 tend to partition to the γ phase, providing a quantitative assessment of elemental partitioning in complex alloys [8]. Notably, the Ni concentration is lower in the matrix (~51%) compared to the γ´ precipitates (~68%).

Atom maps (Fig. 2(a)) reveal that the γ´ precipitates are enriched in Ni, Al, and Ti, whereas the γ matrix is rich in Co and Cr. The corresponding APT reconstruction (Fig. 2(b)), with blue atoms representing element Ti and yellow atoms representing element Al, further illustrates this elemental partitioning.

The γ/γ´ interfaces are delineated by 6.65% iso-concentration surfaces, encompassing regions of ⩾ 6.65. % Al and Ti. A 1-D concentration profile across the γ/γ´ interfaces in the as-cast Al_7Ti_7 MEA (Fig. 2(c)) demonstrates distinct partitioning behaviour, with the γ matrix enriched in Cr (~29%) and Co (~16%), and the γ´ phase enriched in Ni (~68%), Al (11%), and Ti (12%). These findings indicate that Co and Cr preferentially partition to the γ phase, while Al and Ti partition to the γ´ phase, consistent with recent observations [6]. Similar elemental partitioning trends have been observed in other HEAs [7].

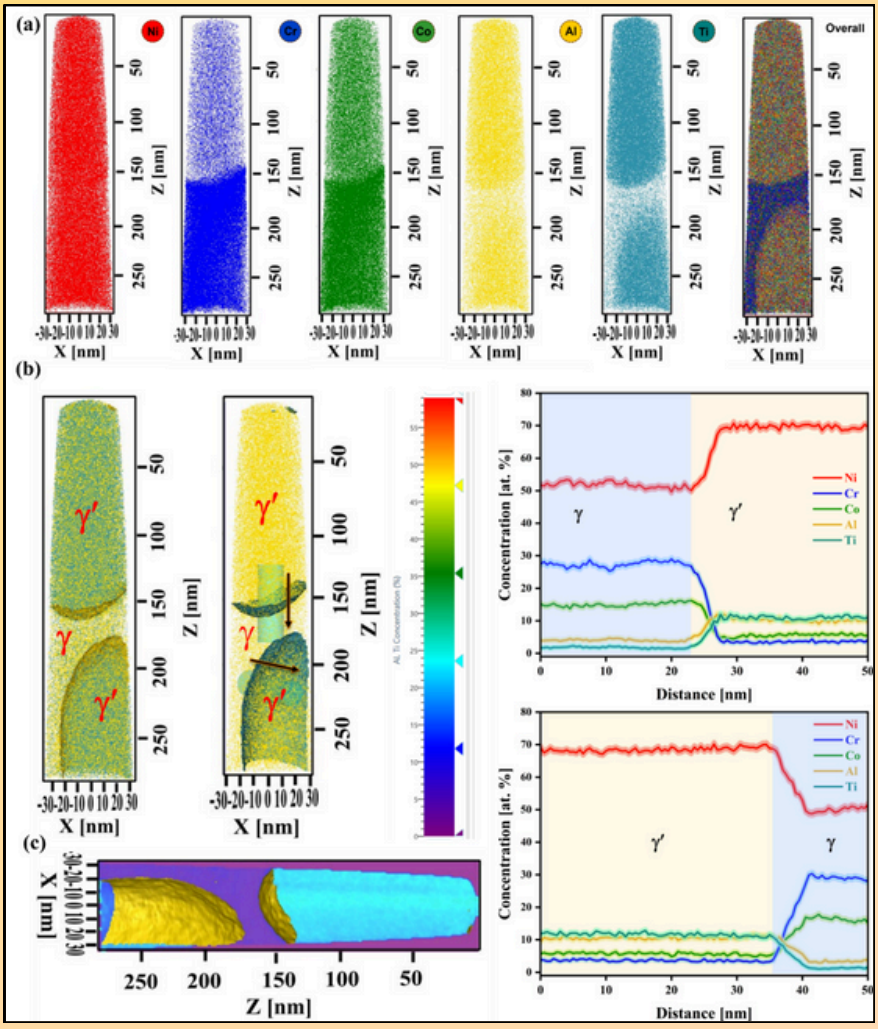

Figure 2: (a) Elemental distribution of Ni, Co, Cr, Al and Ti, (b) Ti delineated using 6.29% Ti iso-concentration surface and distribution Al and Ti with Ti iso-concentration surfaces, (c) one-dimensional concentration profile (0.5 nm bin width) obtained using a 20 nm diameter cylindrical region of interest shown in (b) and (d) 2d concentration plot showing the enrichment of Ti and Al in γ´ phase.

Technique used	Phases	Ni	Co	Cr	Al	Ti	Partition coefficients (Ciγ′/ Ciγ)				
							K_{Ni}	K_{Co}	K_{Cr}	K_{Al}	K_{Ti}
APT	γ′-dendritic	67.12 ±0.21	6.06 ±0.18	3.34 ±0.08	10.32 ±0.13	13.17 ±0.16	1.29	0.39	0.12	3.85	9.14
	γ-dendritic	51.66 ±0.21	15.49 ±0.17	28.74 ±0.21	2.68 ±0.08	1.44 ±0.07					

Table 1: Average chemical compositions of the γ and γ′ phases (at. %) and corresponding partitioning coefficients (K_i), obtained from APT proxigram data.

Precise delineation of individual γ and γ′ phase regions from APT datasets allowed for accurate determination of their phase compositions (Table 1) from the corresponding mass spectra and the calculation of elemental partitioning coefficients. The γ′ phase primarily comprises Ni, Al, and Ti (~ 91%), with the remaining elements accounting for ~ 9%. Among the elements partitioning to γ′ (K_i >1), Ti exhibits the highest partitioning coefficient, followed by Al and Ni, indicating the strongest preference for the γ′ phase. Conversely, Cr and Co preferentially partition to the γ matrix (K_i<1), with Co showing the most significant partitioning coefficient among these elements (Table 1).

The strong partitioning of Ti to γ′ precipitates (K_{Ti}>9) with respect to γ matrix suggests its role as a strong γ′ stabiliser in the alloy. Overall, Ti strongly partitions to γ′, while Cr partitions to the matrix. The total concentration of Co, Cr, and Ni in the γ′ phase approaches ~ 75%, aligning with the stoichiometry of the A_3B-$L1_2$ structure, wherein Co and Ni preferentially occupy the A-sites, and Al and Ti occupy the B-sites. Consequently, the γ′ precipitates in the present alloy can be nominally represented as $(Ni, Co, Cr)_3(Al, Ti)$, which is consistent with the measured composition.

Conclusions:

The APT technique is increasingly recognized as an essential tool for advanced materials characterization. The growing interest in this technique is attributed to its exceptional ability to collect individual ions from nanoscopic volumes, even within complex morphologies, while maintaining single-ion sensitivity and high mass-resolving power.

References:

1. Colliex, C., Nature 450 (2007) 622.
2. Muller, D. A., Nature Materials 8 (2009) 263.
3. Muller, E. W., J Appl Phys 27 (1956) 474.
4. D.G. Brandon, Philos. Mag., 14 (1966) 803.
5. Sujatha Desetti, M. Nagini, D. Arvindha Babu, Dova Kalyan, Surendra Kumar Makineni, Sai Rama Krishna Malladi, B.S. Murty, Submitted, under review, 2025
6. S.C.H. Llewelyn, K.A. Christofidou, V.J. Araullo-Peters, N.G. Jones, M.C. Hardy, E.A. Marquis, H.J. Stone, Acta Mater. 131 (2017) 296-304.
7. S. Adil, M.V. Suraj, P. Lava Kumar, Soumya Sridar, M. Nagini, K.G. Pradeep, B.S. Murty, Mater. 14 (2020) 100909.
8. E. Zaiser, A. Fantin, A.M. Manzoni, R.Hesse, D.M. Tobbens, W.C. Hsu, H. Murakami, A.C. Yeh, M.J. Pavel, M.L. Weaver, H. Zhu, Y. Wu, F. Vogel, Mater. Charact. 220 (2025) 114642.

> *"SATHI-CISCoM is the first centre in the country to enable real-time characterisation across multiple length scales for fundamental and industrial R&D purposes. Through this initiative, scientists from a variety of scientific disciplines, including metallurgy, materials sciences, physical sciences, and chemistry, will come together to address common scientific goals that can only be addressed through the use of sophisticated microscopy techniques."*

[1] Dr Nagini Macha
Senior Scientist, Sathi Ciscom, IITH
[2] Ms D Sujatha
Project Assistant, Confocal Microscopy Lab IITH
[3] Dr Shourya Dutta Gupta
Associate Professor, Dept of MSME
[4] Dr Sai Rama Krishna Malladi
Associate Professor, Dept of MSME
[5] Prof B S Murty
Professor, Dept of MSME