2 PhD scholarship - 2022-2025 :

- **GPM-Rouen :Improving quantification of Nitride and Carbide analyses using Kinetic Energy Sensitive Atom Probe Tomography.**
- **CIMAP-Caen :Simulation of ion-induced electron emission from thin carbon foil**

Improving quantification of Nitride and Carbide analyses using Kinetic Energy Sensitive Atom Probe Tomography.

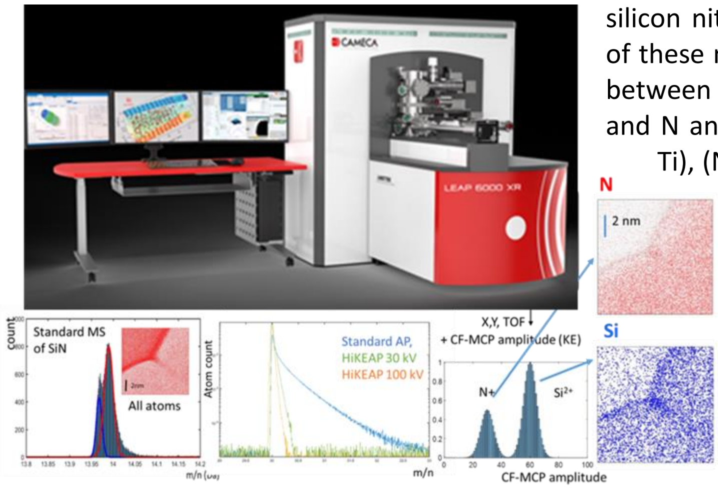
Supervisors	Raphaele Danoix (MCF)		Francois Vurpillot (Prof)	
Starting	September 2022			
Location	GPM UMR CNRS 6634 – Rouen			
Application Deadline	Mars, 30th 2022			
Gross Salary	~2100 €/month			
Funding	*ANR PRCE HiKEAP*		*(GPM/CIMAP/CAMECA)*	
Key Words	*Atom Probe Tomography*	*Artificial Intelligence*	*Nano Analysis*	*Transportation materials*

Context:

Atom probe tomography (**APT**) is nowadays a routine tool for characterization of materials at the nanoscale [LEF16]. The unique capability of this instrument is its ability to provide 3D composition maps of analyzed materials with an extremely high sensitivity (ppm) and a sub-nm resolution. This nano-analysis microscopy technique uses time-of flight (TOF) mass spectroscopy (MS) to identify ions through their mass-to-charge-state ratio (m/n). 3D reconstruction is performed by a two-dimensional (2D) position sensitive detector (PSD) that records ion hit positions and ion TOFs. This technique is well adapted for metals, where only single Me^{n+} ions are evaporated. However, for compounds containing C, N, O, P, S, small molecules are detected. Peaks of different molecules may overlap, making elemental identification cumbersome, and the processing of mass peak interferences requires complex decomposition and deconvolution procedures to achieve at least semi-quantitative composition measurements.

PhD project:

In a **breakthrough ANR PRCE project (Project HiKEAP funded for the period 2022 -2025)**, we propose to evaluate the performance of a prototype new Atom Probe, based on the GPM recent developed of a Kinetic Energy Detector. Performances will be evaluated on the analysis of iron and silicon nitrides and titanium carbides. Mass spectra of these materials all show the presence of overlaps between C/N molecular ions, as well as between C and N and the (semi-)metallic host specie (Si, Fe or Ti), (N_2^{2+} vs. N^+, N^+ vs. Si^{2+}, N_2^+ vs. Fe^{2+}, C_2^{2+} vs. C^+ and C_4^{2+} vs. Ti^{2+}), which limit quantitative composition measurements [BAC13,MAR17]. *These materials were selected as they are not only challenging on a methodological point of view, but also of critical technological importance in the framework of material weight reduction issues currently imposed for the next generation of vehicles. The goal of the project is in fine to validate the prototype of the HiKEAP Instrument.*



Program:

The new prototype instrument will add to TOF mass spectrometry, the capability to measure simultaneously information concerning **Kinetic Energy of detected ions**. A first prototype detector developed at GPM has demonstrated that it is possible to discriminate between singly and doubly charged ions, as their kinetic energy is proportional to their state of charge. This additional information will help discriminating the vast majority of overlapping mass peaks, and thus give access to more quantitative information.

- The first part of the thesis will be devoted to determine the performance of current commercial atom probes on the materials of interest. The selected materials will be analysed on the GPM platform, and with the latest generation of commercial instruments (Invizo® 6000 and LEAP® 6000 for instance, launched in 2022) available at CAMECA Madison.
- A second part of the thesis will be devoted to the development of a new data processing methodology for which preliminary results have been obtained. The thesis will aim to further develop this method and improve the quality of the information extracted from APT data in the case of overlapping multiple peaks. A preliminary investigation has demonstrated that methods based on Bayesian assignation of label through the Expectation – Maximization method enhances the ability to extract information and improve 3D reconstruction quality. The goal is to further develop this method, and to enhance the quality of the information extracted from conventional (non KE) AP in the case of multiple peak overlaps.
- The last part of the thesis aims to analyse the performances of the new APT prototype on the materials of interest, and to compare with the previous results.

Profile: We are looking for a highly motivated student (male or female) holding a master degree or equivalent with a strong background in condensed mater physics or (nano)materials science. Scientific curiosity, strong interest in experimental work and data analysis, written and oral communication skills are required. Knowledge in focused ion beam instruments will be appreciated, even if not mandatory.

Submit your application to
https://emploi.cnrs.fr/Offres/Doctorant/UMR6634-CHRVUR-034/Default.aspx
For more information about the project please email francois.vurpillot@univ-rouen.fr or raphaele.danoix@univ-rouen.fr.

References:

[LEF16] W. Lefebvre, F. Vurpillot, X. Sauvage, Atom probe tomography: put theory into practice, Elsevier, Boston, MA, 2016.

[MAR17] A. Martinavičius, H. P. Van Landeghem, R. Danoix, A. Redjaïmia, M. Gouné, F. Danoix, Mechanism of Si3N4 precipitation in nitrided Fe-Si alloys: A novel example of particle-stimulated-nucleation, Materials letters 189 (2017) 25-27

[BAC13] M. Bachhav, F. Danoix,B. Hannoyer,JM Bassate,R. Danoix, International Journal of Mass Spectrometry, Volume 335, 1 February 2013, Pages 57-60, Investigation of O-18 enriched hematite (α-Fe2O3) by laser assisted atom probe tomography, https://doi.org/10.1016/j.ijms.2012.10.012

[BAC21] C. Bacchi, G. Da Costa1, E.Cadel, F. Cuvilly1, J. Houard, C. Vaudolon, A. Normand and F. Vurpillot, Development of an energy-sensitive detector for the Atom Probe Tomography, submitted to M&M 2021, preprint available in arXiv:2103.04765

Contrat de thèse / PhD 2022-2025

Amélioration de la quantification des analyses des nitrures et carbures en sonde atomique tomographique sensible à l'énergie cinétique.

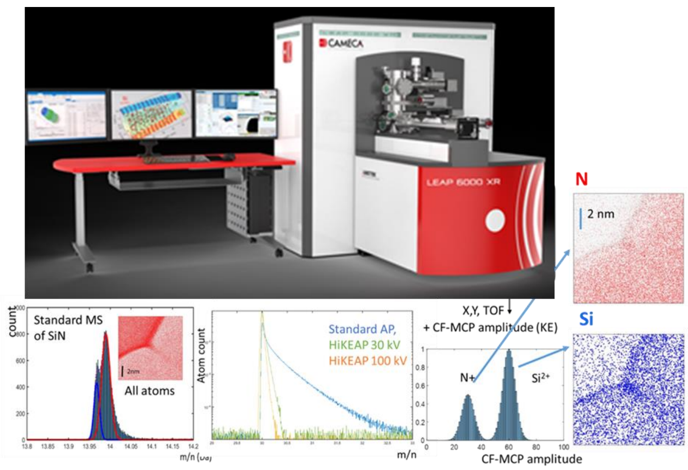
Encadrement	Raphaele Danoix (MCF)		Francois Vurpillot (Prof)	
Démarrage	Septembre 2022			
Lieu	GPM UMR CNRS 6634 – Rouen			
Deadline	Mars, 30^{th} 2022			
Salaire Brut	~2100€/mois			
Financement	*ANR PRCE HiKEAP*		*(GPM/CIMAP/CAMECA)*	
Mots Clés	*Sonde Atomique Tomographique*	*Intelligence artificielle*	*Analysis à l'échelle nanométrique*	*Carbures nitrures*

Contexte

La sonde atomique tomographique (APT) est aujourd'hui un outil de routine pour la caractérisation des matériaux à l'échelle nanométrique [LEF16]. L'originalité de cet instrument est sa capacité à fournir des cartes de composition 3D des matériaux analysés avec une sensibilité extrêmement élevée (ppm) et une résolution inférieure au nm. Cette technique de microscopie et de nano-analyse utilise la spectroscopie de masse (MS) à temps de vol (TOF) pour identifier les ions grâce à leur rapport masse/état de charge (m/n). La reconstruction 3D est effectuée grâce à un détecteur sensible à la position (PSD) bidimensionnel (2D) qui enregistre les positions d'impact des ions et les TOF des ions. Cette technique est bien adaptée pour les métaux, où seuls les ions Men+ simples sont évaporés. Cependant, pour les composés contenant du C, N, O, P, S, de petites molécules sont aussi détectées. Les pics de différentes molécules peuvent se chevaucher, ce qui complique l'identification élémentaire, et le traitement des interférences de pic de masse nécessite des procédures complexes de décomposition et de déconvolution pour obtenir au moins des mesures de composition semi-quantitatives.

Projet de doctorat :

Dans le projet ANR PRCE (Projet HiKEAP financé pour la période 2022 -2025), nous proposons d'évaluer les performances d'un prototype de nouvelle sonde atomique, basée sur le détecteur à capacité de mesure d'énergie cinétique récemment développé au GPM. Ses performances seront évaluées par l'analyse des nitrures de fer et de silicium et des carbures de titane. Les spectres de masse de ces matériaux montrent tous la présence de chevauchements entre les ions moléculaires contenant C et/ou N, ainsi qu'entre C et N et l'espèce hôte (semi-)métallique (Si, Fe ou Ti), (N2_2+ vs N+, N+ vs . Si_2+, N2+ vs Fe2+, C2_2+ vs C+ et C4_2+ vs Ti2+), qui limitent les mesures quantitatives de composition [BAC13, MAR17]. *Ces matériaux ont été sélectionnés car non seulement ils se révèlent difficiles à analyser d'un point de vue méthodologique, mais aussi car ils sont d'une importance technologique capitale dans le cadre de la problématique de l'allégement des matériaux de structure actuellement imposée pour la prochaine génération de véhicules.* L'objectif final du projet est de valider le prototype de



l'instrument HiKEAP par les mesures sur ces nitrures et carbures.

Programme:

Le prototype du nouvel instrument ajoutera à la spectrométrie de masse classique, la capacité de mesurer simultanément des informations concernant l'énergie cinétique des ions détectés. Un premier prototype de détecteur développé au GPM a démontré qu'il est possible de discriminer les ions simplement chargés des ions doublement chargés, car leur énergie cinétique est proportionnelle à leur état de charge. Ces informations supplémentaires aideront à discriminer la grande majorité des recouvrements des pics de masse, et donneront donc ainsi accès à des informations plus quantitatives.

- La première partie de la thèse sera consacrée à la détermination des performances des sondes atomiques actuelles sur ces matériaux d'intérêt. Les matériaux sélectionnés seront analysés sur la plateforme du GPM, et avec la dernière génération d'instruments commerciaux (Invizo® 6000 et LEAP® 6000, lancés en 2022) disponible à CAMECA Madison.
- Une seconde partie de la thèse sera consacrée au développement d'une nouvelle méthodologie de traitement de données pour laquelle des résultats préliminaires ont été obtenus. La thèse aura pour but de développer davantage cette méthode et d'améliorer la qualité des informations extraites de la sonde actuelle dans le cas de chevauchements de pics multiples.
- La dernière partie de la thèse a pour but d'analyser les performances du nouveau prototype de sonde sur les matériaux d'intérêt, et de comparer avec les résultats précédents.

Déposer votre dossier de candidature ici
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Pour plus d'information contacter francois.vurpillot@univ-rouen.fr ou raphaele.danoix@univ-rouen.fr

Profil du candidat :
Nous recherchons un étudiant ou une étudiante très motivé(e) avec une solide expérience en physique de la matière condensée, en science des (nano)matériaux ou similaire, et titulaire d'un master ou équivalent (diplôme d'ingénieur par exemple). Une curiosité scientifique, un fort intérêt pour les travaux expérimentaux et l'analyse de données, des compétences en communication écrite et orale sont requis. Des connaissances en techniques de caractérisation telles que MET, spectroscopie électronique ou spectrométrie ionique seront appréciées mais non obligatoires.

Refs :

[LEF16]W. Lefebvre, F. Vurpillot, X. Sauvage, Atom probe tomography: put theory into practice, Elsevier, Boston, MA, 2016.
[MAR17]A. Martinavičius, H. P. Van Landeghem, R. Danoix, A. Redjaïmia, M. Gouné, F. Danoix, Mechanism of Si3N4 precipitation in nitrided Fe-Si alloys: A novel example of particle-stimulated-nucleation, Materials letters 189 (2017) 25-27
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Simulation of ion-induced electron emission from thin carbon foil

In the framework of the HIKEAP project funded by the French ANR, we investigate a new detector for tomographic atom probe (TAP). The project is a collaboration between the GPM (Rouen), CAMECA and the CIMAP (Caen). The TAP metrology is based on ion field emission from a very thin tip of a material to be analysed, with a curvature radius of several ten of nanometers. The ions emitted from the tip are detected with a localization detector and the time of flight between the tip and the detector allows the experimentalist to identify the chemical nature of the ion. The time of flight is directly linked to the mass over charge ratio. There are unfortunately some cases where this ratio is not sufficient to discriminate unambiguously the emitted ion. This is the case for example for N^+, which we cannot discriminate from the molecular ion N_2^{2+}. This is also the case for O^+ and S^{2+}, or for D^+ et H_2^+.

To overcome this limitation, the GPM develops a new kind of detector based on ion-induced electron emission from very thin carbon foil located in front of the detector. The number of emitted electrons is sensitive to the projectile velocity and two different ions with the same time of flight could be discriminated. At CIMAP, we shall simulate numerically the emission process to estimate the best operation conditions of the new instrument. It will help us to choose the best carbon foil thickness and potential acceleration to identify with the highest possible confidence the incoming ion. To reach this goal, we will perform a Monte Carlo simulation of the ion transport through the foil and of the resulting electron emission. Such a method allows us to obtain the distribution of the number of emitted electron for such a complex phenomenon.

During this project, we shall investigate systematically a series of atomic projectiles characterized by their atomic number Z and mass M and a kinetic energy E ranging from 10 to 100 keV, for carbon targets characterized by their thickness t ranging from 1 to 100 $\mu g.cm^{-2}$ (approximately 5 to 500 nm). Following previous works in the field of electron emission, we shall consider the electron generation as a two-step process. First, the projectile propagates through the target. Then the electrons knocked by the projectile propagate through the target and eventually stop in the target or are emitted. The electron transport is uncorrelated from the projectile transport, i.e. an electron does not anymore experience projectile interaction once it has been sent in motion. These two aspects of electron emission are taken into account to setup an event-by-event Monte Carlo (MC) simulation code to predict ion transmission and associated electron emission. In such a code, the inputs are given by the cross sections, which define the probability of occurrence of a given event. These probabilities are sampled to form Markov chains of events, which are associated to a given number of emitted electrons, n, and the transmission or non-transmission of the projectile through the carbon foil. A large number of such Markov chains need to be realized numerically to produce statistically meaningful data. The relative number of Markov chains ending with emission of n electrons defines the probability $p(n)$ for transmitted and non-transmitted projectiles.

The simulation has to be ran for each projectile characterized by its composition, charge and energy and for the whole range of target thicknesses. This represents of course a large amount of data and it is desirable to achieve a handy description of them and to interpolate between computed points. Therefore, after running the simulations, we will derive a user-friendly code which will return an interpolation of $p(n)$ for any given set of parameters (Z, E/M, t) in the above defined range. Such a code will be extremely useful to explore target thickness or acceleration potential variations. The task of CIMAP team is thus the development of such a user-friendly code, which requires more exchange with the other partners.

The funding is for 36 months, and will start current 2022. A previous experience in simulation and in code development using C language is necessary. A good knowledge of atomic structure theory, collision theory and statistical physics is mandatory. The student will work in the SIMUL team of CIMAP (5 permanent researchers + PhD and postdocs) in Caen (Normandy, France) and will have regular exchange with experimentalist in GPM, CAMECA and CIMAP.

Contact: B. Gervais - gervais@ganil.fr