



## Editorial

One major 2022 highlight has been the 15<sup>th</sup> anniversary of our Institute. We warmly thank CNRS and UPEC as well as our academic and industrial partners for their continuous support over this period. ICMPE is now well established at the national and international levels with three areas of expertise, namely materials for energy and transport, materials and processes for sustainability, and chemistry for healthcare.

Since January 2022, ICMPE has been coordinating an important project focused on the stationary storage of hydrogen in solid media within the framework of the national PEPR H2 2022-2026 program under the auspices of CNRS and CEA. This year a French-Ukrainian international research project on high-temperature resistant polymeric materials based on synthetic and natural phenols has also been launched under the auspices of CNRS and the National Academy of Sciences of Ukraine. The latter projects are two significant examples of the diverse research themes developed in our laboratory. Other typical examples are illustrated in this Newsletter by five original articles on machine learning, nanoporous materials, biosourced polymers, thermoelectric materials, and metallic alloys.

**Daniel Grande** ICMPE Director • **Ivan Guillot** Deputy Director



*Michel Latroche, Director of Research at CNRS and former director of ICMPE from 2012 to 2019, passed away on December 30, 2021. Expert in the field of energy materials, Michel Latroche was an outstanding solid-state chemist and crystallographer, internationally recognized for his work on hydride-forming intermetallics for electrochemical and solid-gas hydrogen storage. Author or co-author of about 300 research papers, regularly invited to speak at international conferences, his scientific visibility has earned him*

*numerous national and international recognitions (e.g., Vice-Chair of the Gordon Research Conference in 2019, expert for several national and international authorities). Carrying numerous projects in collaboration with industrial partners, he had been responsible for more than 60 research contracts, 11 patents, and multiple international collaborations worldwide (Brazil, Canada, China, Japan, Tunisia, USA, ...). He regularly talked in national media (La Recherche, France Culture, France 2, Les Echos).*

*In 2022, we were also saddened to lose Annick Percheron-Guégan, former director of the Laboratoire de Chimie Métallurgique des Terres Rares at the CNRS in Meudon and then in Thiais from 1992 to 2004, and of the Institut des Sciences Chimiques Seine-Amont (2004-2006), the federative structure before the creation of the ICMPE in 2007. Annick established herself as a well-known international expert in the field of materials science of intermetallic hydrides focusing on studying structure-properties relationships dedicated also to their use as anodes of metal hydride batteries. Her works are comprehensively covering various aspects of the studies of AB<sub>2</sub> type hydrides, with a major focus on LaNi<sub>5</sub>-related compounds. Already in 1977, she presented a talk on "Hydrogen Electrochemical Storage by Substituted LaNi<sub>5</sub> Compounds" at a pioneering conference in Norway. Annick also organized various conferences, including the Int. Symposium on the Properties and Applications of Metal Hydrides V (Mauvoisin, 1986), Int. Symposium on Metal Hydrogen Systems (with D. Fruchart in Annecy, 2002) and the Gordon Conference on Hydrogen in Metals in 2003 (with M. I. Baskes, USA). As a director of the LCMTR, she received the award Équipe de Recherche de l'Année from CNRS and Le Nouvel Economiste journal in 1995. She was distinguished as Chevalier de la Légion d'Honneur in 2009.*



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## Newsletter

December 2022

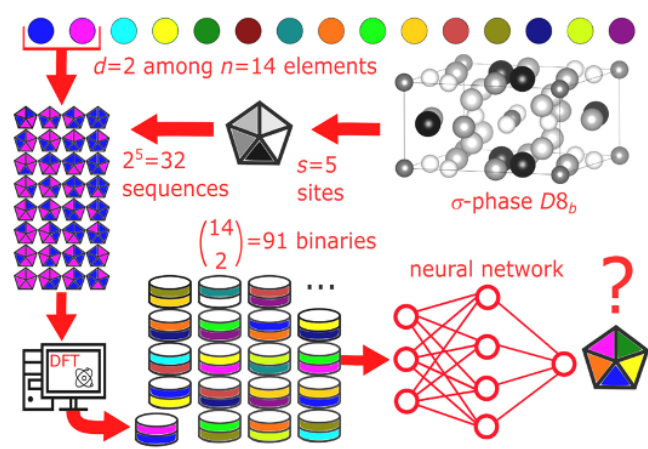
### Machine learning

#### Supervised deep learning prediction of the formation enthalpy $\Delta_f H$ of the complex $\sigma$ phase

This work addresses the issue of the crystal phase stability from the machine learning viewpoint. Because the  $\Delta_f H$  is the key descriptor to model the formation of compounds, the prediction of this variable has been investigated using a supervised approach, within a complex crystallographic structure as an example: the  $\sigma$  phase.

Based on an unprecedented large first-principles dataset containing about 10,000 compounds with  $n = 14$  different elements, several supervised learning approaches have been optimized, among which the neural network shows best results to predict all the 14<sup>5</sup>~500,000 possible configurations within a mean absolute error of ~2 kJ mol<sup>-1</sup> on the testing set.

It is shown that the training database from the only binary-combinatorial compositions (only 0.5% occurrence of the whole set) can predict higher degree system configurations with a high accuracy. This result suggests that several complex phases including non-equivalent sites could be easily determined from the only binary contribution and opens a broad avenue to efficient high-throughput computations for multicomponent intermetallic phase prediction.



J.-C. Crivello, J.-M. Joubert, N. Sokolovska, *Comput. Mater. Sci.* **2022**, 201, 110864. [↗](#)

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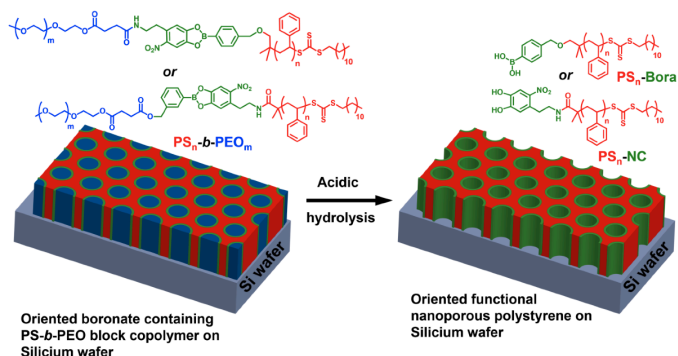
# Nanoporous materials

## Functional nanoporous materials from boronate containing stimuli-responsive diblock copolymers

Oriented nanoporous polymers obtained from block copolymers represent a class of materials possessing a great potential in various applications, especially in the fields of energy storage/conversion, heterogeneous supported catalysis, and separation technology.

We report on a convergent synthetic strategy allowing for the preparation of functional nanoporous materials obtained from novel polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) diblock copolymer precursors containing a reversible boronate ester junction between both blocks. To this purpose, homopolymers end-capped either a boronic acid or a (nitro)catechol functionality were first synthesized. The coupling of each homopolymer presenting complementary chemical functions was successfully achieved under mild conditions and allowed for the generation of the corresponding boronate ester-containing diblock copolymers. Upon orientation of these precursors on silicon wafers *via* solvent vapor annealing, the resulting films were submitted to PEO etching through selective cleavage of the boronate ester junction under mild acidic conditions. SEM micrographs of the as-obtained thin films revealed the generation of 12 nm-diameter oriented cylindrical nanopores perpendicular to the silicon support surface.

These new nanoporous polymers notably present at the pore surface either boronic acid or catechol functional groups that could be promising candidates to envision potential applications, particularly in the field of supported catalysis.

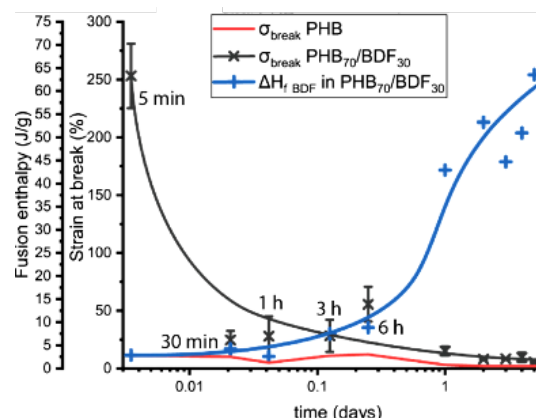


E. Bakangura, D. Fournier, F. Coumes, P. Woisel, D. Grande, B. Le Droumaguet. *Polym. Chem.* **2022**, 13, 2907. [↗](#)

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# Biosourced polymers

## Improved processability and antioxidant behavior of poly(3-hydroxybutyrate) in the presence of ferulic acid-based additives



L.F. Longé, L. Michely, A. Gallos, A. Rios De Anda, H. Vahabi, E. Renard, M. Latroche, F. Allais, V. Langlois, *Bioengineering*, **2022**, 9, 100. [↗](#)

Since their production method was streamlined a few decades ago, poly(3-hydroxyalkanoate)s (PHAs), which are produced by a fermentation process, have shown a growing amount of interest. Indeed, PHAs are one of the most promising renewable biocompatible and biodegradable polyesters. Produced by microorganisms in presence of natural substrates, they offer an excellent alternative to petroleum-based plastics.

In this work, three novel additives based on ferulic acid esterified with butanediol, pentanediol, and glycerol (BDF, PDF, and GTF, respectively) were used as plasticizers and antioxidative additives to improve mechanical properties of PHB. Elongation at break up to 270% was obtained in presence of BDF and the processing window was improved nearly 10-fold. The Pawley method was used to identify the monoclinic space group P2 of the BDF. The estimated crystallite size (71 nm) agrees with a crystalline additive. With PHB<sub>70</sub>BDF<sub>30</sub> blends, even higher elongations at break were obtained though dwindled with time.

The reversibility of the mechanical properties according to the temperature combine with the antioxidant properties and the resistance to the flammability will undoubtedly allow to consider new applications for the PHB.

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## Past events

- The plenary sessions of the **Hydrogen Research Federation** took place in Aussois from May 30<sup>th</sup> to June 3<sup>rd</sup>, 2022. Contact: Fermin Cuevas, co-leader of the Storage act of the FRH<sub>2</sub>.

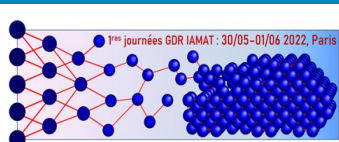
- The **first plenary meeting of the GDR "Artificial Intelligence in Materials Science"** took place at Sorbonne University from May 30<sup>th</sup> to June 1<sup>st</sup>, 2022, under the auspices of the National Institutes of Physics and Chemistry of the CNRS. Its mission is to bring together the many teams and communities interested in artificial intelligence approaches in materials science (theoretical and experimental). Contact: J.-C. Crivello, co-organizer



- An **international day on Hydrides and Energy Storage** was dedicated to the memory of **Michel Latroche** on June 13, 2022, at ICMPE, in presence of his wife and one of his daughters. It was supported by the *Institut National de Chimie* of CNRS, the *Université Paris-Est Créteil*, the French Research Network for Hydrogen Energy (FRH<sub>2</sub>) and ICMPE. Many of Michel Latroche's national and international collaborators, all internationally recognized in their field of expertise, paid tribute to him and gave their personal testimonies on his achievements in the fields of solid-state chemistry, hydrogen and electrochemical energy storage.

- We had the pleasure of hosting Prof. Mitra Taheri, from the Department of Materials Science & Engineering at Johns Hopkins University, who gave a seminar entitled *Atomic Legos: From atoms to machines and back again*, on Monday June 20, 2022.

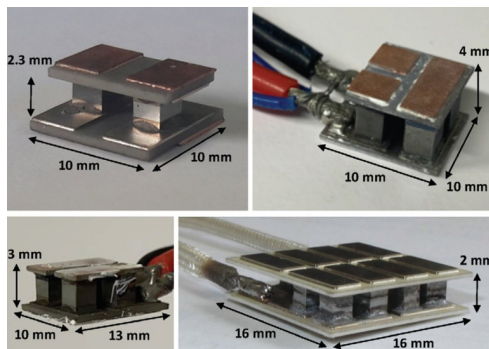
- The 13th Japan-France joint seminar on "Lithium Batteries and New Generations" was held from July 4 to





# Thermoelectric materials

## High Power Density Thermoelectric Generators with Skutterudites



S. El Oualid, I. Kogut, M. Benyahia, E. Geczi, U. Kruck, F. Kosior, P. Masschelein, C. Candolfi, A. Dauscher, J. D. Koenig, A. Jacquot, T. Caillat, E. Alleno and B. Lenoir, *Advanced Energy Materials* **2021**, 11, 2100580. [↗](#)

Thermoelectric (TE) materials can directly convert a temperature difference into electrical power, offering a versatile way to recover energy from any heat source. Skutterudites are iron – cobalt antimonides, which lead to thermoelectric generators with improved efficiency ( $\geq 10\%$ ). To reduce their manufacturing cost, TE generators designed with decreased quantity of active materials and still able to generate large output power are required.

This goal cannot be reached by only decreasing the volume of the bar-shaped TEM: it also implies decreasing both the electrical contact resistance between the skutterudites and the copper electrode which collects the electrical current and the mechanical stresses induced by temperature. In the present work, these issues have been tackled by inserting a metallic layer (Ti/Cu composite) between the skutterudites and the joining to the copper electrode. This new design, combined with high-performance skutterudites ( $\text{In}_{0.2}\text{Co}_4\text{Sb}_{12}$  and  $\text{Ce}_{0.8}\text{Fe}_3\text{CoSb}_{12}$ ) synthesized with reproducible TE properties, led to a record value of output power:  $7.6 \text{ W cm}^{-2}$  under a temperature difference of 630 K. This achievement corresponds to a 60-fold decrease of the volume of skutterudites compared to the literature.

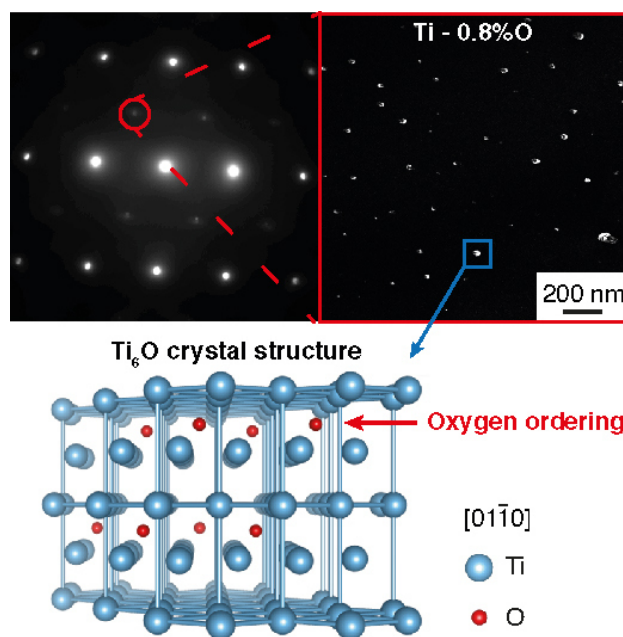
Contact : [eric.alleno@cnrs.fr](mailto:eric.alleno@cnrs.fr)

# Metallic alloys

## First experimental evidence of oxygen ordering in dilute titanium–oxygen alloys

Small addition of oxygen is currently used to improve the mechanical properties of titanium. It has been thought, until now, that oxygen fully dissolves in the titanium matrix, thus leading to a solid solution. However, we show here, with transmission electronic microscopy and X-ray diffraction, that oxygen can also form ordered precipitates with a  $\text{Ti}_6\text{O}$ -type structure, even for a concentration as low as 0.15 wt% O. The ordered precipitates found in a series of pure binary Ti–O alloys are also visible in commercially pure titanium, including grades 2 and 4, two compositions widely used for technological applications.

Oxygen-ordered precipitates are experimentally evidenced in a series of Ti–O alloys and in CP titanium. These findings question the paradigm defining oxygen only as a solute atom in titanium alloys.



R. Poulain, S. Delannoy, I. Guillot, F. Amann, R. Guilloud, S. Lartigue-Korinek, D. Thiaudière, J.-L. Béchade, E. Clouet, F. Prima, *Mater. Res. Lett.* **2022**, 10, 481-487. [↗](#)

Contact : [regis.poulain@cnrs.fr](mailto:regis.poulain@cnrs.fr)

7 in Provins. J.-P. Pereira-Ramos, R. Baddour-Hadjean, G. Bernari from ICMPE were the organizers on the French side.



- To celebrate its **15<sup>th</sup> anniversary**, ICMPE organized a scientific day on Thursday, July 7. Invited and local researchers presented their work in a festive atmosphere.

- ICMPE organized the **FERMI Federation Science Day** which took place on December 9, 2022 on its campus. The theme was "Crystal Growth and Single Crystals". Academic and industrial speakers addressed topics related to crystal solidification and all types of applications and properties (crystals for optics, particle detection, super alloys, refractory materials...).



- To celebrate the arrival of the Laboratoire de Géographie Physique (LGP) on the CNRS campus in Thiais on July 2022, the **1<sup>st</sup> joint seminar between ICMPE and LGP** was organized on December 12, 2022.

## Distinctions

- Congratulations to **Julie Fouilloux**, 2<sup>nd</sup> year PhD student in C3M department who won the Jury Prize for the presentation of her thesis on antibacterial filtration systems at the 8<sup>th</sup> Paris-Est Sup finals of "My Thesis in 180 seconds" competition (March 15, 2022).
- Kudos to **Tania Xavier** who received the 2022 University Prize for her PhD thesis in chemistry from UPEC entitled: "Use of eco-designed reagents: Biosourced dienes by valorization of coumalates & bio-inspired nucleophiles". This prize is yearly awarded by the Val-de-Marne (94) Department in order to support scientific research by rewarding the best University works of the 94 Department.

## Welcoming our new faculty and staff members



● We are pleased to introduce **Géraldine Dieutegard** who has taken on the position of General Secretary of ICMPE and is responsible of its administrative department since December 1<sup>st</sup>, 2022.

● ICMPE is delighted to be joined by four members of the former team "Physique des Liquides et des Milieux Complexes" (PLMC) of UPEC who will integrate the modeling group of M2I department in January 2023 as

physicists/digital scientists: **Abderrahime Ayadim** (MCF, FST), **Philippe Germain** (MCF, Inspé), **Lucas Levrel** (MCF, Inspé) and **Jean-Guillaume Malherbe** (MCF-HDR, FST).

● We welcome **Régis Poulain** as a new assistant professor at UPEC. He graduated from ESPCI, then he prepared his PhD thesis at IRCP and received his diploma from the "Paris Science et Lettres" University. He worked for two years at ICMPE and UPEC as an ATER. He will now be working in the M2I Department on the optimization and characterization of the microstructure in metallic alloys, and particularly in alloys designed for permanent magnets.



● We are also pleased to welcome **Romain Moury** who has been appointed junior professor of the NOMASH (New Materials for Hydrogen Storage) chair at UPEC for 5 years. Romain obtained his PhD diploma at the University of Montpellier, and then spent post-doctoral stays at the Max Planck Institute (Germany), at the University of Geneva (Switzerland) and at the *Institut des Molécules et Matériaux du Mans*. He has joined the M2I department of ICMPE to work on complex hydrides for energy storage.

● ICMPE is proud to have 19 new PhD students at the end of 2022 (+54% vs. last year!), 3 ATER, and 2 post-doctoral researchers: Dr. H. Chaliyawa from India (ANR SIROCCO, 18 months, *Photoelectroreduction of CO<sub>2</sub>*), and Dr. A. Batia (European Contract, 12 months, *Batteries*).

## ICMPE acknowledges contributions of its members in writing books, chapters and review articles

- D. Grande and B. Le Droumaguet wrote a chapter entitled "Porous Polymers by Block Copolymer Templating" in *Macromolecular Engineering: From Precise Synthesis to Macroscopic Materials and Applications*, 2nd Edition; Matyjaszewski, K., Gnanou, Y., Hadjichristidis, N., Muthukumar, M., Eds.; John Wiley & Sons: Hoboken, NJ, 2022.
- A review article entitled "Contribution of the "Click Chemistry" Toolbox for the Design, Synthesis and Resulting Applications of Innovative and Efficient Separative Supports: Time for assessment" was published by B. Le Droumaguet, M. Guerrouache and B. Carbonnier in *Macromolecular Rapid Communications*, 2022, 2200210.
- A review entitled "New materials for hydrogen storage - Multi-principal alloys forming hydrides" in *Les Techniques de l'Ingénieur* by C. Zlotea (Ref: IN403 v1).
- A review article entitled "Metallic and complex hydride-based electrochemical storage of energy", coordinated by Michel Latroche, and published in *Progress in Energy* 2022, 4 032001, presents the state of the art of research on innovative metal or complex hydride materials in the field of solid electrolytes and anodes for alkaline and ionic batteries.

## Scientific communication

- On June 17, 2022, E. Torralba did a scientific visio-demonstration to children in 5<sup>th</sup> year of education at the Primary School "Maestro Joaquín Cantero" in Murcia (Spain), focused on Energy Conversion and Instruments: 1- Presentation of ICMPE and demonstration of solar energy conversion (solar cells, water electrolysis, fuel cell); 2- Presentation of Apparatus built by

students, questions/answers; 3- Instruments at ICMPE: Induction furnace for Cu fusion presented by V. Lalanne; Spark Plasma Sintering for bulk pyrophoric materials synthesis presented by B. Villeroy.

## New research projects funded in 2022

- In the framework of PEPR H2, the **SOLHYD** project on stationary storage of hydrogen in solid media is coordinated by Fermin Cuevas (ICMPE-M2I). It brings together 1 UPR CNRS, 5 UMR CNRS / University and 2 units of CEA, with the recruitment of 6 PhD students and 1 post-doctoral fellow and a budget over 1 M€ for ICMPE.
- Within the US project "From Percolation to Passivation: Multiscale Prediction and Interrogation of Surface and Oxidation Phenomena in Multi-Principle Element Alloys," **MURI P2P**, ICMPE (J.-P. Couzinié, M2I) was selected to collaborate with John Hopkins University for the preparation of complex alloys. Pr. Taheri (PI) and 3 PhD students visited ICMPE on June 2022 for 20 days to perform experiments on these alloys
- **ECaSep**, MOF-decorated polymer monolith in sequential microcolumn for Enantioselective Catalysis and in-line Separation in continuous flow, B. Carbonnier (ANR PRC)
- **BISTIPLEX**, Bicontinuous non-equilibrium Structures stabilized by Interfacial Polymer complexation, A. Mikhailovskaya (ANR JCJC)
- **BIO-ART**, Optimization of Mechanical Properties of BIO-sourced Epoxy Resins by ARTificial Intelligence, E. Renard (PRCI France-Germany)
- **TACTIC**, Aerosol-assisted synthesis of spherical mesoporous cerium oxide particles as stimuli-responsive nanoCarriers for theranostic, S. Belbekhouche (PRCI France-Germany)
- **AIIM**, Artificial Intelligence for Intermetallic Materials, responsible scientifique : J.-C. Crivello (PRCI France-Germany).

## Upcoming workshops and conferences

- There will be a Summer School: Materials to Technologies for Advanced Energy Storages (MATES) in Bordeaux, from July 4 to 7, 2023, organized by the University of Bordeaux, the Quebec Center for Advanced Materials and the French-Australian network IRN FACES co-directed by Fermin Cuevas (ICMPE).

## They update their business card

- Sylvie Lartigue, CRHC CNRS, and Léo Mazerolles, DR2 CNRS, retired after their long and successful careers at CNRS, especially at the *Centre d'Études de Chimie Métallurgique* (CECM, Vitry-sur-Seine), one of the laboratories that merged to create ICMPE and to which they contributed greatly. We wish them a great time in retirement!
- Davy-Louis Versace, UPEC associate professor has been promoted to full professor of chemistry at the UPEC.

## Carbon footprint

ICMPE carried out its first Carbon footprint assessment (year 2019) as part of a CNRS initiative with the support of Labos1.5, a transversal collective of researchers aiming to better understand and reduce the environmental impact of research.

The Institute's footprint was equal to 1300 tons of CO<sub>2,eq</sub> in 2019, with 3 main sources of CO<sub>2</sub> emissions: energy for 67% (heating being the main item), purchases and services for 23%, and travels (commutes + scientific travels) for 8%. The heating of buildings (oil-fired boiler) is the main source of CO<sub>2</sub> emissions, accounting for 60% of the total.

However, green-house gas emissions will be greatly reduced from 2022 and on, thanks to a major thermal renovation of all the buildings on the ICMPE campus financed by CNRS. In addition, the CNRS "Délégation Régionale Ile-de-France Villejuif" has been awarded a "Resilience" project from the Government's French Recovery Plan, enabling ICMPE to change its old oil-fired boiler for a wood pellet boiler. All this should allow ICMPE to reduce by at least 50% its Carbon footprint by next year.

## New equipment

ICMPE has been granted 1.6 M€ to increase its microscopy facilities (CPER 2022-2026) ● ICMPE has just acquired a Bridgman type directional solidification furnace (ECM Greentech, France) for the crystal growth of metallic alloys, which completes the metallurgical manufacturing facilities.

## Tribute

It is with great sadness that we learned of the passing of our former colleague Jean-Yves Duot, who had just retired last year. He made his career as a technician at CNRS, formerly at the *Centre d'Études et de Chimie Métallurgique* and since 2007 at ICMPE. Our thoughts are with his family and friends.

## ICMPE Publication

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