

focus on Microscopy & Microtechniques

Investigating the Plasticity of a Colloidal Polycrystal at the Laboratoire Charles Coulomb, CNRS/University of Montpellier 2

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The University of Montpellier 2 is a distant descendent of two medieval universities that are among the oldest in Europe. It is a member of the Coimbra network, which brings together some forty ancient European universities of the Latinus network, a network of the higher education establishments of the Latin world, and of the Agency for French-Speaking Universities (Agence Universitaire de la Francophonie - AUF). The Soft Condensed Matter Group of the Laboratoire Charles Coulomb is composed of 13 research fellows and faculty members, 5 post-docs and 8 graduate students.

At the University of Montpellier 2, the Colloidal Metallurgy Team, part of the Soft Condensed Matter Group of the Laboratoire Charles Coulomb and led by Principle Investigator: Laurence Ramos, CNRS scientist, is designing a colloidal polycrystal system (using polymers and colloids) to get a model for molecular or atomic polycrystals that will permit a better understanding of the mechanical and plastic properties of polycrystals. The aim of the team is to relate the macroscopic mechanical properties to the microscopic texture of the polycrystal, thanks to a combination of advanced experimental techniques, including light and neutron scattering, optical microscopy, rheology, which allow one to probe the matter at different scales (from nanometer and micrometer to macroscopic length scales).

The Colloidal Metallurgy project, which is funded by both the Agence Nationale de Recherche (ANR) and the Centre National de la Recherche Scientifique (CNRS), is motivated by open issues in atomic systems and in metals in particular. Indeed, most solid materials in everyday life are crystals, whose constituents (atoms, molecules...) are regularly positioned in space. However, all real-life crystalline materials have defects, which strongly affect their properties. Moreover, most metals and ceramics are polycrystals, i.e. aggregates of crystalline grains with different size and different lattices orientation (texture of the polycrystal). Grain-boundaries (GBs) are two dimensional defect lattice that separate the different grains. GBs control the bulk mechanical properties of polycrystalline materials: in particular, the sliding and the migration of GB play important roles in the plastic deformation and the fracture at high temperature. In the group's project, they propose to use a colloidal analogue of atomic polycrystals. The colloidal system is transparent and so observable with a confocal microscope (doping the system with fluorescent nanoparticles) and with light scattering. By combining the visualisation of the 3D GB structure and mechanical measurements (confocal microscopy + CSS450), the team will be able to collect space-time resolved information on the local dynamics of the crystallite organisation under an applied shear strain. These measurements in direct space will be complemented by those obtained from a novel apparatus that combines an original space-time resolved dynamic light scattering method with simultaneous mechanical measurements (light scattering setup + CSS450). In both cases, by varying the crystallisation rate, the team will be able to investigate how the mechanisms at play depend on the crystallites' size. As they will have access to the local shear deformation and GB dynamics, they expect to elucidate the different microscopic mechanisms that play in the plasticity of polycrystals.

To summarise, the current project on colloidal metallurgy takes advantage of the much larger characteristic length and time scales, much softer elasticity, and the optical transparency of a colloidal polycrystal as compared to atomic crystals to obtain unprecedented space- and time-resolved information on the deformation of a polycrystal under load. By using a unique colloidal analogue of atomic polycrystals, the team will elucidate the different mechanisms at play, at a microscopic level, in the plasticity of polycrystals, these processes being still largely unknown.

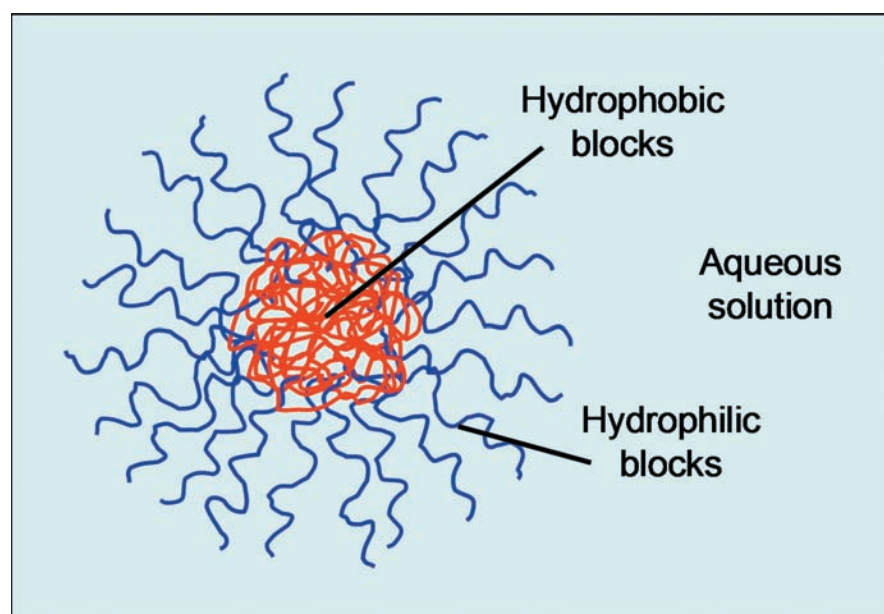


Figure 1. An example of micelles in polar solvent (Water, in this case)

The developed colloidal model is constituted by micelles of a commercial molecule: Pluronic F108 block copolymer. Pluronic block copolymers are also known under the name "poloxamers" and consist of hydrophilic poly(ethylene oxide) (PEO) and hydrophobic poly(propylene oxide) (PPO) blocks arranged in A-B-A tri-block structure. In aqueous solutions at concentrations above critical micelle concentration (CMC) these copolymers self-assemble into micelles with an average diameter of ca. 10nm to 100nm.

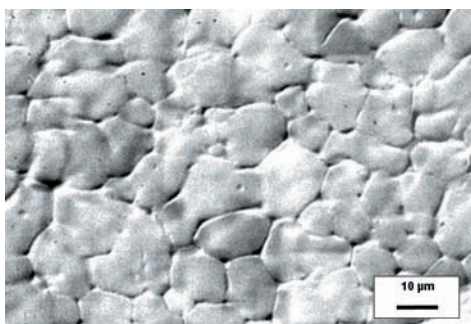


Figure 2. Differential interference contrast (DIC) microscopy image of a Pluronic polycrystal. The system is made of Pluronic F108 32% w and silica nanoparticles 1% v with diameter 30 nm in water. The crystallisation is reached with a temperature ramp of 0.007°C/min. It is clear that, during the crystallisation, silica nanoparticles are expelled from the crystal lattice and decorate the GBs, permitting the scientists to visualise them with a microscope.

in the grain-boundaries of polycrystalline soft materials allows their visualisation by light or confocal microscopy, an expedient used by the team to image the texture of the polycrystal.

The team investigates by small-angle neutron scattering (SANS) the structure of water-based soft composite materials comprising a crystal made of Pluronic block-copolymer micelles (diameter ~ 22nm) arranged in a face-centred cubic lattice and a small amount (at most 2% volume fraction) of silica nanoparticles, of size comparable to that of the micelles [1]. The team uses contrast-variation experiments to probe independently the structure of the nanoparticles and that of the polymer. They find that the nanoparticles do not perturb the crystalline order. In addition, a structure peak is measured for the silica nanoparticles dispersed in the polycrystalline samples. This implies that the samples are spatially heterogeneous and comprise, without macroscopic phase separation, silica-poor and silica-rich regions. They show that the nanoparticle concentration in the silica-rich regions is about 10 fold the average concentration. These regions are grain boundaries (GBs) between crystallites, where nanoparticles concentrate, as confirmed by light microscopy imaging of the samples and by static light scattering.

The team takes advantage of a specific property of the copolymer used. The copolymer is thermo-sensitive: it is hydrophilic and fully dissolved in water at low temperature ($T \sim 0^\circ\text{C}$), and self-assembles into micelles at room temperature, where the block-copolymer is amphiphilic. The team has shown that the speed at which the sample is brought from a fluid phase (at low T) to a crystalline phase (at room T) influences the size of the crystallites in the polycrystals, as shown in the two pictures. Nanoparticle concentration has also been shown to influence crystallite size [2].

The team complement SANS data by light scattering measurements at lower scattering vectors, q , covering almost three decades in q and so detecting the signal coming from the GBs. Such a large range in q is obtained by combining static light scattering (SLS), small angle light scattering (SALS) and ultra-small angle light scattering measurements (USALS). Static light scattering measurements have been performed using a goniometer and the USALS setup is a common ultra small angle light scattering setup. To cover the q range between SLS and USALS measurements, a unique small angle light scattering set up has been designed and built in such a way that the range of detectable angle is 0.5 deg - 26

The hydrophobic PPO blocks form the core of the micelles, separated from the aqueous exterior by the hydrophilic PEO chains. These copolymers display surfactant properties including ability to interact with hydrophobic surfaces and biological membranes due to their amphiphilic character. It is also well known that if the number of formed micelles is sufficiently high, they are packed to form a crystalline phase of micelles in water. F108 micelles are therefore the equivalent of atoms in an atomic crystal, except that they are two orders of magnitude bigger.

Nanoparticles are added to the block copolymer solutions. They are the equivalent of impurities in atomic systems and in particular in metallic alloys. As such, they are expelled from the crystalline phase and segregate in the grain-boundaries. Confinement of nanoparticles

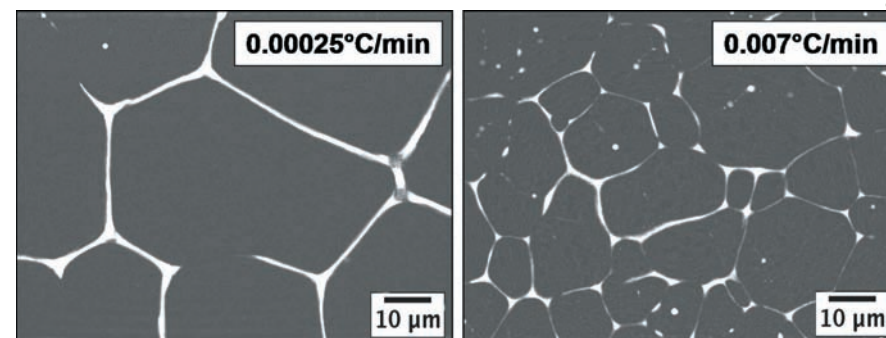


Figure 3. Confocal microscopy image of a Pluronic polycrystal. The system is made of Pluronic F108 34% w and polystyrene fluorescent nanoparticles (0.5% volume fraction) with diameter 36nm in water. The sample is brought from the fluid phase to the crystalline phase by increasing the temperature with prescribed rate, 0.00025°C/min and 0.007°C/min.

deg (a common set up reaches 10 deg). In this SALS apparatus it is also possible to perform dynamic light scattering measurements at all angles in the detectable range.

Placing a shear cell (Linkam cell CSS450) instead of a common light scattering cell, the team is able to perform dynamic light scattering measurements on the sample under shear to study its mechanical properties. Other measurements on the sample under shear were done using the CSS450 on a confocal microscope. The data analysis is ongoing.

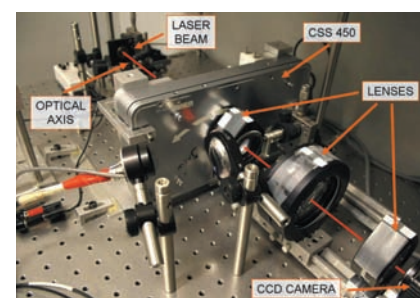


Fig. 4. CSS450 Linkam stage in SALS apparatus.

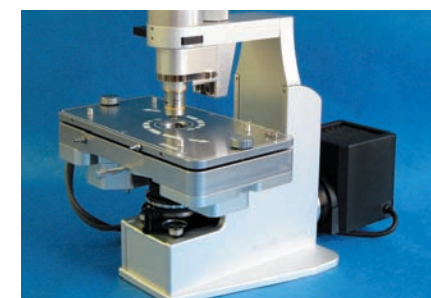


Fig. 5. CCS450 Stage with Imaging Station

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