

## 3 - MATERIALS SCIENCE

Materials science is a scientific field at the crossroads of physics, chemistry and engineering sciences, which aims at understanding how parameters such as chemical composition, atomic structure and microstructure determine the macroscopic properties of complex solid systems (alloys, polymers, geological materials...). The scientific productions and conclusions of this broad field of research have short-term consequences on the day-to-day applications and often concern plain industrial research.

The research in materials science covers two main domains :

- 1) Research on ill-condensed matter including liquids, glasses and disordered systems and
- 2) Metallurgy for which, the main research topics are focussed on the analysis of the residual stresses and the determination of crystallographic textures.

The LLB approach of materials science includes a particular attention to industrial needs and problems, but also a fundamental character in particular through the analysis of the mechanical behaviour of micro-heterogeneous materials, the study of crystallographic textures, the analysis of structural heterogeneities and the phenomena of precipitation as well as ageing in metal alloys.

The last part of this material section presents the structural studies of Polymorphs and Solvates of Fullerenes and research on molecular compounds.

### **Metallurgy**

#### **Residual stresses**

(M. Ceretti, R. Levy, A. Menelle, LLB ; A. Lodini, University of Reims Champagne-Ardenne)

Internal and residual stresses in materials have a considerable effect on material properties, including fatigue resistance, fracture toughness and strength. Neutron diffraction provides a powerful non-destructive tool for stress analysis deep within a crystalline material. The principle of the technique, called Neutron Strain Scanning, is to use the crystal lattice as an atomic strain gauge to measure strain distributions with a sub-millimetre spatial resolution. The stresses are thus calculated from the measured strains using the well-known elasticity laws. The G5.2 diffractometer dedicated to the strain characterization has been improved in the past years, in particular with a new sample stage based on three coupled elevators (with a 300 mm extension range) controlled by three potentiometers. Mercury switches are installed under the upper table to insure the horizontality of the table during measurement. The precision in the position is of the order of 10µm. The new device (table +columns) is also equipped with a XY-table, each translation with a total course range of 150 mm. This device can handle very big samples, up to 500 kg in weight, with a good positioning precision and consequently presents a real interest for industrial applications.

Engineering activity at the LLB has significantly developed in the last two years. A large number of real industrial problems have been studied in collaboration with academic and industrial partners.

Among the principal industrial contracts, the work carried out in collaboration with DASSAULT Aviation can be mentioned. In the frame of a large research programme aimed to control the conception and the structural behaviour of fighter plane units, neutron diffraction has been used to characterize the residual stress fields in a representative wing of a MIRAGE 2000.

In the field of materials used in the aeronautics sector, neutron diffraction found a new application in the analysis of the residual stresses after a welding carried out by a very promising new process in rapid development : the Friction-Stir Welding (FSW) technique ("Highlight" of Stelmukh et al.).

Furthermore, the collaboration with SNCF concerning the evaluation of the residual stresses at the interface between the wheel and its axis has been continued and completed by finite element calculations. This work represents a large part of the thesis of A. Yameogo ("Highlight").

The diffraction technique gives elastic strain values averaged on the diffracting volume, but the materials can present heterogeneous strains between grains (different phases or crystallographic orientations) or in the grains (fluctuations). The experimental data analysis is therefore based on averaging techniques and scaling methods such as the well-known homogenisation method. The comparison between experimental and theoretical results allows to validate a model and to determine the effective properties of micro-heterogeneous materials. These approaches constitute a field of research presently under very active development because of the expected applications. In particular, the study of the inter and intragranular

elastic strain distributions in a Dual-Phase Steel was continued in collaboration with LMS (J. Crépin, D. Caldemanon, Ecole Polytechnique, Palaiseau, France) and LPMTM (O. Castelnau, N. Letouze, University of Villetaneuse). This material presents a very anisotropic local behaviour, for which every elastic loads induce a heterogeneous strain field. "In situ" neutron diffraction measurements, in the elastic range, have been realized adapting the loading machine of LMS. The measurements of in-situ peak broadening at different elastic loads allowed characterising the increase of strain heterogeneities, which are comparable with theoretical homogenisation predictions.

### Crystallographic textures

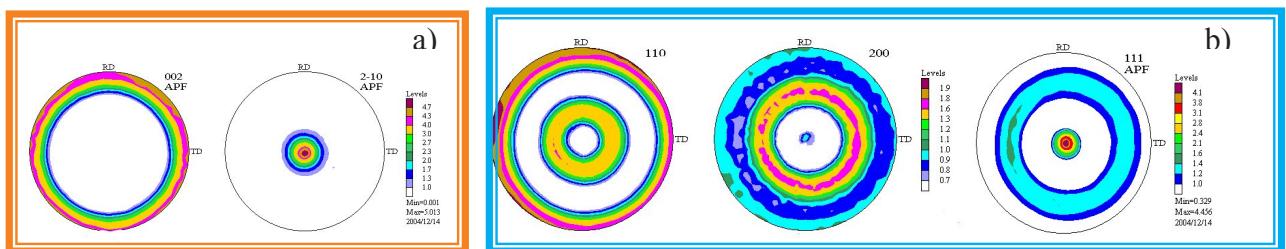
(M.H. Mathon, P. Gerber, S. Jakani, C.H. de Novion, LLB; T. Baudin, A.L. Etter LPCES, Orsay University)

Crystallographic texture (preferential orientation of the grains) is one of the parameters describing the microstructure of a polycrystalline material, which controls partly its mechanical properties. In metal alloys, texture appears during solidification, then changes during stages of working (rolling, wiredrawing) and finally during the recrystallization.

Neutron diffraction is the best technique to determine the crystallographic texture of massive polycrystalline specimens (Volume  $\sim 1 \text{ cm}^3$ ), in the form of a crystalline orientation distribution function. Its use is in particular necessary in the case of large grains materials (few  $\text{mm}^3$ ) frequently met after primary or secondary recrystallization, for which the diffraction of conventional X-rays is not applicable.

The LLB has a 4-circles diffractometer dedicated to texture measurements, "6T1" on which, a furnace has been recently adapted on the Euler's cradle (see "Highlight") allowed to performed "in situ" measurements at high temperature (up to  $1000^\circ\text{C}$ ). The possibility of carrying out an "in situ" texture analysis as a function of temperature, allows on the one hand to quantify the kinetics of formation or disappearance of the components, and on the other hand to understand the evolution of the preferential orientations during phase transformations.

Such a procedure represents a major asset for the textures study at high temperature in zirconium alloys within the framework of the development of a predictive model for the cladding tubes and guide tubes behaviour in accidental situation in Pressurized Water Reactors (PWR). For the first time, measurements were performed at room temperature and at  $900^\circ\text{C}$  to determine respectively the hexagonal  $\alpha$  phase components and the centered cubic  $\beta$  phase texture (see figure 1). They have shown that the main texture components follow the burger's law ( $(110)\beta//(00.2)\alpha$  &  $[-1-1]_\beta//[-2-1.0]\alpha$ ) in agreement with models. This study has been performed in collaboration with J.L. Béchade (CEA/DEN/SRMA). This protocol has been also applied to titanium alloys in collaboration with J. Delfosse (MSSMat, École Centrale Paris).



**Figure 1 :** Pole figures measured on the  $\alpha$  hexagonal phase at room temperature (a) and on the  $\beta$  cubic centered phase at  $900^\circ\text{C}$  (b). Some of them (2-10 for  $\alpha$  and 111 for  $\beta$ ) have been calculated from the Orientation Distribution Function to exhibit the burger's law.

A large part of the crystallographic texture activity is always dedicated to the recrystallization phenomena study in various materials (FeNi, two-phase alloys, etc.). More precisely, several works have for main goal to understand in face centered cubic alloys, the development, during the recrystallization, of a strong "cube" component  $\{100\}<001>$  beyond a critical deformation rate. The determination, from the diffraction peaks broadening, of the stored energy by the grains during the deformation, had highlighted that the grains of cubic orientation stored an energy lower than the grains belonging to the other preferential orientations (see the preceding activity report). The "in situ" follow-up of the preferential orientations during the recrystallization annealing brings additional information on the kinetics. For that, the diffracted intensity variation is followed versus time at various temperatures, for particular poles corresponding to deformation components that will disappear or on the contrary, to recrystallization components which will develop. From

the increase of the scattered intensity at the centre of the {100} pole figure, the activation energy of the recrystallization phenomena has been determined in cold rolled copper. It has been done for two rolling deformation rate (70 and 90 % reduction). Energy values respectively close to 34 and 24 k/mol have been found. These results can be correlated with the stored energy values determined previously in this material. Indeed the higher is the stored energy and consequently the driving force of recrystallization, the lower is the activation energy. These experimental activation energy determinations bring fundamental data to be introduced in statistically recrystallization models actually developed in the laboratory.

This parametric study has been realized in wire-drawn copper in the context of the "OPEFiC" research project partly subsidized by the French Research Ministry, including 3 laboratories (LLB, LPCES, LPMTM of Villeurbanne University) and 2 French producing copper wire rod companies (SCCC, SLC). The main objective of this project is to study the residual impurities (S, Pb) effect on the deformation and recrystallization mechanisms in order to understand the wire ductility decrease observed after thermomechanical (wiredrawing followed by heating) treatments. The "OPEFiC" research project has been the framework of S. Jakani thesis (see "Highlight"). This study has shown that the presence of the impurities in very low contents modifies the substructure of deformation (dislocations cell) and the total stored energy. The mechanisms of recrystallization are not modified but the kinetics is slow down because of a delay in the recovery phase as well as the decrease of the grain boundaries mobility in the presence of impurities.

### **Study of heterogeneities, Precipitation**

(M.H. Mathon, C.H. de Novion, LLB; Y. de Carlan, A. Alamo, J.L. Béchade CEA/SRMA)

The studies of heterogeneities and of precipitation phenomena are integrated in various themes and are primarily based on Small Angle Neutron Scattering (SANS) experiments. These studies cover a large number of subjects and are the matter of collaborations in particular with the Laboratoire de Chimie du Solide Minéral (University of Nancy) concerning the ageing of Pb-Ca-Sn alloys used in the Pb accumulators and with the Ecole des Mines (Albi). This last collaboration with D. Delagnes et al. focus on the study of tool steels whose mechanical resistance is controlled by the dislocation distribution induced in the material during the quench treatment and by the carbide secondary precipitation produced during the tempering. TEM observations and SANS experiments were performed in order to analyse the carbides population evolution after a double tempering and a fatigue test in two steels containing respectively 1 wt-% and 0.35 wt-% of silicon. A considerable effect of silicon on the secondary carbides precipitation has been shown throughout a higher volume fraction of small secondary carbides (mainly vanadium carbides) in the low-silicon steel. The precipitation sequence is in fact modified and as a consequence, the secondary hardening peak of the low silicon grade is shifted towards higher temperatures.

These last years, many experiments were devoted to the study of ageing and of microstructural evolutions under neutron irradiation or thermal ageing in materials of nuclear interest.

In particular, the studies concerning the 7-12% Cr martensitic steels - candidates for the internal structure of future generation reactors or spallation sources – were continued. It was shown that when the Cr content of the b.c.c. ferritic matrix was larger than a critical threshold value ( $\sim 7.2$  at.% at  $325^\circ\text{C}$ ), the ferrite separated under neutron irradiation into two isomorphous phases, Fe-rich ( $\alpha$ ) and Cr-rich ( $\alpha'$ ). The quantity of precipitated  $\alpha'$  phase increases with the Cr content and the irradiation dose. The Cr solubility limit in iron at the irradiation temperature, was deduced from this study and we can conclude that the only effect of neutron irradiation is to speed up the precipitation.

A new study in collaboration with CEA/SRMA (J.L. Béchade, S. Doriot) concerns the microstructural evolution under neutron irradiation of Zr alloys used for cladding tubes. More precisely, SANS experiments were performed to provide quantitative and statistical information on the radiation-enhanced precipitation of  $\beta$ -Nb needles and possible other defect or solute clusters in two different industrial alloys (Zy4 used in REP and Zr-2.5%Nb). These experiments have pointed out a significant increase of the radiation-enhanced precipitation with the radiation dose (between 1.5 and 3 PWR cycles) as well as a notable modification of the precipitates shape that changes from a quasi spherical form to an elliptic one. Moreover, the formation of defects clusters of small size (coherent with dislocations loops) was observed.

Finally, a significant share of the activity in SANS domain was devoted to the study of oxides dispersion strengthened materials (ODS) worked out by mechanical alloying. The data treatment is under way.

## **ill-Condensed Matter and New Technologies for Clean Energy**

Neutron scattering is an essential technique for the study of disordered systems in general and, more specifically for the investigation of structural and dynamic properties of molecular liquids and glasses. This is essentially due to the possibilities of isotopic substitution and of incoherent scattering. Among the many studies undertaken in these fields of research, we will quote examples of experiments performed at LLB on the diffuse scattering diffractometer 7C2 and on the time-of-flight inelastic spectrometer MIBEMOL.

Parallel to the experimental works, molecular modelling is developed at the LLB and applied to the diffraction and scattering data interpretation in the research field of molecular compounds.

### **Study of liquids and glasses**

(B. Beuneu, M.C. Bellissent-Funel, LLB ; B. Belhorma, CNESTEN Maroc)

There is a growing interest in structural studies of multi-component oxide glasses by means of neutron scattering, which are now a large part of the “disordered systems” studies. *First*, because, due to their complexity, the structural role of the various oxides is not yet clear, and in glasses of industrial use, it is of great importance to understand how each added oxide modifies the properties of the material. *Second*, because the recent simulation techniques (reverse Monte Carlo and molecular dynamics) open new fields to the analysis of the diffraction data of these complex materials with a well-defined short-range order. The other experimental techniques (NMR, Raman, Mossbauer, ...) give good information about the first co-ordination shell, but Neutron techniques can go much further in the reciprocal space and gather some information on medium range order, which can be extracted throughout these simulations.

With a group of the University of Rennes 1 (Deriano, Rouxel et al.), we had first studied the effect of nitrogen on the structural properties of high mechanical performance silicate glasses. Neutron diffraction combined with NMR has shown how nitrogen was increasing the benefit of adding magnesium for the mechanical properties: nitrogen helps magnesium to enter the network as a precursor in tetrahedral sites, which increases the bond strength of Mg-O. This collaboration is continuing (including now F. Lofaj from the Institute of Materials Research of SAS, Slovakia), through the study of silicate glasses which simulate the grain boundary phases of high temperature ceramics: the rheological properties of these ceramics are driven by this vitreous intergranular phase.

The structure of oxide glasses and liquids is also of great interest for the earth science, since they enter as a large part in the composition of the earth mantle. A group of the Laboratoire de Minéralogie-Cristallographie (L. Cormier, O. Majerus, G. Calas, et al., Université Paris 6) has undertaken a systematic study of the structural changes with temperature in some oxide glasses, by means of neutron diffraction studies which strongly imply the LLB, combined with X-ray diffraction, NMR, Mossbauer, or EXAFS measurements. Model cases of two-oxide glasses have been studied (alkali diborate glasses, which can be also a model for nuclear waste containment glasses, and alkali disilicate glasses). Diffraction data were taken on 7C2 at different temperatures from 300K to 1350K ( $T_g \approx 700\text{-}850\text{K}$ ). The environment of Li was investigated using isotopic substitution. The pronounced change with temperature of the alkali environment is the main common features of the two studies. And although the atomic order decreases with temperature, a marked medium range order remains in the liquid phase. A detailed analysis of the K disilicate glass results by means of Reverse Monte Carlo and Molecular Dynamics simulations has shown that the FSDP (first sharp diffraction peak), that increases at high temperature, can be explained by correlations between well polymerised network domains surrounding K rich domains.

In addition, the interaction of trivalent neodymium ions with nitrate ions and neutral organic molecules is investigated in concentrated solution of  $\text{Nd}(\text{NO}_3)_3$  dissolved in  $\text{C}_2\text{D}_5\text{OD}$ . Neutron scattering experiment combined with the first-order isotopic-difference method was applied to  $\text{Nd}^{3+}$  to determine the local order around  $\text{Nd}^{3+}$  ions. The results show that the trivalent neodymium ions have a coordination number between 8 and 9. The first salvation shell is composed of ethanol molecules and nitrate ions at distances of 2.26 Å and 2.45 Å respectively (“Highlight”).

### **New Energies : the fuel cell systems and batteries**

The fuel cells make possible a direct conversion of chemical energy into electric power. They are different according to the nature of their electrolyte and by the level of their operating temperature, their architecture and the applicability in which each type can be used. Cell systems, whose electrolyte is an membrane promoting the exchange of protons, concentrate a significant share of the world effort of research and

development on New Technologies of Energy (NTE). Converting today's oil based, inefficient and polluting transport technology into a more sustainable equivalent is a tough challenge. Proton Exchange Membrane Fuel Cells (PEMFC) will very likely play an important role by offering silent and emission-free electrical power for our future vehicles.

In this context, a study using the quasi-elastic neutron scattering was carried out at the LLB by J.C. Perrin, S. Lyonnard, O. Diat and G. Gébel (LPCI, CEA Grenoble) to study ionomer membranes. The ionomer membranes, such as the Nafion, are complex materials exhibiting a hierarchical structure, organised from the angstrom to the millimeter. They are characterized by a nanophase separation between hydrophobic and hydrophilic domains; their properties, notably the protonic conductivity, strongly depend on the water content. The study of the protonic diffusion mechanisms, and more generally the water management in these membranes, requires the use of many experimental techniques that cover a wide range of relaxation times, from the picosecond to the second. In addition to NMR spectroscopy and macroscopic characterisations, the quasi-elastic neutron scattering technique allows to investigate the proton dynamics at the molecular level. Two series of experiments performed on the spectrometer Mibemol allowed to study the elementary processes of diffusion in the Nafion as a function of the Relative Humidity (RH). Two types of motion have been identified : the first one corresponds to a fast local diffusion in a confined volume, the size of which increases (from 5 to 10 Å) when increasing the water amount, up to an 80% RH value. The second type of motion is a long-range diffusion, which has been surprisingly observed already in the very early phases of hydratation. The Nafion do not behave as a typical "porous" material : it percolates immediately, and, beyond 80% RH, the structure swells very significantly without any modification of the underlying elementary dynamical processes. The neutrons are particularly well suited to study these perfluorinated polymers, the contrast with water being excellent. Two experiments on complementary spectrometers (spin-echo and backscattering) are programmed to reach longer relaxation times.

In the same field of "clean" energy, the influence of confinement on polymer-electrolyte relaxational dynamics was studied by J.-M. Zanotti (LLB and IPNS, Argonne) et al. In terms of stored energy and safety, solid-state devices using polymer electrolytes are highly desirable. One of the most studied systems is PEO (polyethylene oxide) complexed by Li salts. Polymer segmental motions and ionic conductivity are closely related. Bulk PEO is actually a biphasic system where an amorphous and a crystalline state ( $T_g \approx 213$  K,  $T_m \approx 335$  K) coexist. To improve ionic conduction in those systems requires a significant increase of the amorphous phase fraction where lithium conduction is known to mainly take place. Confinement strongly affects properties of condensed matter and in particular the collective phenomena inducing crystallization (*International Workshop on dynamics in confinement, edited by B. Frick, R. Zorn and H. Buttner, Journal de Physique, 10, PR7 (2000)*). Confinement of the polymer matrix is therefore a possible alternative route to the impractical use of high temperature.

Results of a quasi-elastic incoherent neutron scattering study of the influence of confinement on polyethylene oxide (PEO) and  $(\text{PEO})_8\text{Li}^+[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$  (or (POE)<sub>8</sub>LiTFSI) dynamics are presented. The nano-confining media is Vycor, a silica based hydrophilic porous glass (characteristic size of the 3D pore network  $\approx 50$  Å). As expected, the presence of Li salt slows down the bulk polymer dynamics. The confinement also affects dramatically the apparent mean-square displacement of the polymer. Local relaxational PEO dynamics is described by the Kolhrausch-Williams-Watts (KWW) model. We also present an alternate model and show how the detailed polymer dynamics (correlation times and local geometry of the motions) can be described without the use of such stretched exponentials so as to access a rheology-related meaningful physical quantity: the monomeric friction coefficient (*Zanotti et al., Macromolecule, submitted*). Such a quantity could be an effective way to accurately estimate the viscosity of confined or interfacial polymer and/or polymer electrolytes.

$\text{Li}_2\text{O}$ , a superionic conductor of interest in the context of solid state batteries, has been studied after electron irradiation by elastic diffuse neutron Huang scattering. The team of Krexner et al., (see the corresponding "Highlight") showed the formation under irradiation of Li precipitates which were characterised regarding their size, concentration, shape and defect strength.

## **Structural Studies of Polymorphs and Solvates of Fullerenes and other Molecular Compounds of Industrial or Pharmaceutical Interest**

Initiated two years ago at LLB by Papoular, and carried out in collaboration with Prof. R. Céolin [Faculté de Pharmacie, Univ. Paris 5] and Prof. V. Agafonov [Faculté de Pharmacie, Univ. Tours ], this new line of research involves molecular modeling and mostly X-Ray diffraction techniques. Molecular Modeling (using the commercial Hyperchem and Spartan softwares) is essential to obtain chemically sound structural restraints to be used in the GSAS-based Rietveld refinements of the powder diffraction data.

### ***Polymorphs and solvates of fullerenes***

(R.J. Papoular, LLB ; R. Céolin, P. Espeau, Paris 5 ; H. Allouchi, Tours ; J.-Ll. Tamarit, Barcelone)

A variety of hexagonal C<sub>60</sub> polymorphs and hexagonal/cubic C<sub>60</sub> solvates [with various solvents like CH<sub>4</sub>, CH<sub>3</sub>CCL<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub> and C<sub>9</sub>H<sub>20</sub>] has been investigated by high-resolution X-ray powder/single-crystal diffraction as well as by thermodynamic measurements, namely thermogravimetric and differential scanning calorimetric studies, both at room and low temperatures. Modeling plays a key role in the obtention of ab initio structure solutions derived from the powder diffraction spectra. Results are currently being published [*Chem. Phys. Lett., 2004, Carbon, 2005* ].

The C<sub>60</sub>.CH<sub>2</sub>Cl<sub>2</sub> solvate has been measured using both X-Ray and Neutrons [*J.Phys.IV, 2005*]. It is described briefly as one of the “highlights” that follow this introduction.

### ***Preferential adsorption of n-alkanes on Graphite***

(P.Espeau, Paris 5 ; R.J. Papoular, LLB)

Monolayers of mixtures of n-alkanes [ C<sub>15</sub>H<sub>32</sub>-C<sub>17</sub>H<sub>36</sub>, C<sub>16</sub>H<sub>34</sub>-C<sub>17</sub>H<sub>36</sub>, C<sub>15</sub>H<sub>32</sub>-C<sub>16</sub>H<sub>34</sub>] adsorbed on graphite [papyex] have been studies by very Small Angle X-ray Scattering (SAXS). The preferential adsorption of the longer chain [ C<sub>17</sub> vs C<sub>15</sub>, C<sub>17</sub> vs C<sub>16</sub> ] has been evidenced, and a simple theoretical formalism developped to account for it. These results are now published [*Applied Surface Science, 2005*]. Further work involves the detailed analysis of the 2D diffraction peak, which is characteristic of adsorbed monolayers. Albeit being strongly asymmetric, the observed experimental lineshape does not follow the widely-accepted Warren form [1941] that has been modified to account for the X-ray diffraction measurements.

### ***Polymorphism of gamma- Butyrolactone [ BL ]***

(R.J. Papoular, LLB ; H. Allouchi, V. Agafonov, D. Lemordant, Tours; A. Dzyabchenko, Moscow)

Both an important industrial compound for Li batteries but also a pharmacological agent, gamma-Butyrolactone is a liquid at room temperature that crystallizes into one of two polymorphs [BL1, stable ; BL2, metastable ] at low temperature. The BL1 polymorph has been solved and refined at 180 K in the monoclinic system, whereas the BL2 polymorph crystallizes in the triclinic system (XRPD studies). Preliminary results are now published [*Acta Crystallogr. B, 2005*].

Extensions of this work currently in progress involve :

- i) understanding the connection between the liquid and the solid phases and
- ii) refining the triclinic BL2 phase (8 independent molecules), which may require synchrotron data.