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, ceramics, composite materials, polymers, geological materials...). The scientific repercussions of this work have short-term consequences on the applications and interest industrial research.

Neutron radiation proves to be an ideal probe to analyse the structure of many materials because of the weak absorption of neutrons, allowing analyses on large volumes and in complex or extreme conditions (temperature, loading...), and because of the advantageous neutron-matter interaction to differentiate some chemical elements. The activity in materials science developed at the LLB are focussed on the analysis of the residual stresses including an approach with industrial needs, 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, the mechanisms of martensitic phase transitions and the phenomena of precipitation as well as ageing in metal alloys.

1. RESIDUAL STRESSES

The residual stresses present in a material have a considerable influence on its mechanical properties, such as hardness and mechanical resistance, tenacity or fatigue strength. Neutron diffraction is a powerful tool to determine in a non-destructive way the internal stresses in a massive crystalline material. The principle of the technique is the use of the crystal lattice as a strain probe at the atomic scale, allowing to map the strain distribution with a submillimeter space resolution. The stresses are then calculated from the measured strains, applying the linear elasticity laws. At the LLB, the "DIANE" (G5.2) diffractometer installed on the cold neutron channel G5, is dedicated to stress measurements. It has been built in collaboration with INFM (Italy). The stress activity developed at the LLB, at the border of technological interest studies and of research in the field of physical metallurgy, is led in several directions:

- Studies or expertises, in relation with problems encountered by the industrialists;
- Mechanics of heterogeneous materials;
- Development of the peak broadening analysis.

The activity of LLB in Engineering Sciences has significantly increased since the last years. Concerning the residual stresses, several industrial problems were studied, in general within the framework of contracts, or by the means of European programs (in particular TRAINSS).

TRAINSS network and residual stress in metal-matrix composites

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

Among the main **industrial collaborations** of the 2001-2002 period, let us mention the work carried out with SNECMA. This study concerns Ti-SiC blings considered for replacing the discs of compressors by SNECMA Moteurs. In this composite material, the residual thermal stresses, resulting from the differences in thermal expansion coefficient between the two phases, can have significant consequences during in-service operation. Neutron diffraction makes it possible to separately determine these stresses in each phase of the composite, and in-depth in a non-destructive way on the whole ring. The measurements were performed on this component just after its elaboration and after fatigue tests at 20°C. They showed that the Ti matrix presents, on all the thickness, a homogeneous state of stresses in tension and that the SiC reinforcement is in compression (490 ± 40 MPa and –920 ±80 MPa respectively for the circumferential stress measured after the elaboration). After the fatigue test, a decrease of the residual stress level is observed for the two phases (360 ± 30 MPa and –660 ± 60MPa, respectively for the Ti matrix and the SiC). After a fatigue test at higher temperature (450°C, 800MPa, 100 000 cycles), the residual deformations are two times lower than just after the elaboration.

TRAINSS was a European network of the Brite-Euram III program (1998-2001), implying several neutron sources and universities, and intended to train industrialists to the use of neutron diffraction for internal stress determination. Within this framework, specific problems submitted by the SNCF and PSA-Peugeot-Citroen were studied at the LLB. The SNCF was interested by the influence of the residual stresses on the crack propagation at the interface between the wheels and their axis, caused by oligocyclic fatigue in rotational bending. An experimental set-up was developed implying an entry hole to decrease the absorption of the incident neutron beam during the measurements. The measured strains at the wheel-axis interface are in agreement with the predictions of calculations carried out by finite elements. The work performed in the frame of TRAINSS should be extended and broadened to the synchrotron radiation within the 6th EU Framework Program Integrated Project IMPRESS ("Improved safety and reliability through applicable neutron and synchrotron strain scanning"), currently in fulfilment.

*Residual elastic strains in natural Quartzite samples (“**highlight**”)*

Since several years, neutron diffraction has been used to study the residual elastic strains and the crystallographic textures in quartzite samples which are relevant for the **understanding of the thermomechanical history of geological materials** (J. C. Guézou, Université Cergy-Pontoise), see “***Highlight***”).

*Mechanical properties of heterogeneous materials (see also the two related “**highlights**”)*

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

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 grain heterogeneities are considered as “phases” with different mechanical behaviours. The experimental data analysis needs the use of scale change 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 intense development because of the expected applications; they lead to a better description of the material’s mechanical behaviour laws and constitute simultaneously an invaluable tool for new materials development. From its high penetration depth in matter and the possibility of distinguishing the various phases, the neutron probe is an ideal tool for a structural study of heterogeneous materials such as polycrystals with coarse grains (heterogeneity of plastic strain), composites with metal matrix, multiphase materials… Several studies of fundamental character have been performed at LLB to understand the mechanical behaviour of such **heterogeneous materials**:

- Experimental residual stress analysis in both phases of a metal matrix composite Al/SiC submitted to various types of strains, has allowed to determine the necessary input physical parameters and to **validate a self-consistent elastoplastic model**, which was shown to give a very accurate prediction of the mechanical properties of the material (see “***Highlight***”).
- In collaboration with LMS (J. Crépin, D. Caldemaison, Ecole Polytechnique, Palaiseau, France) and LPMTM (O. Castelnau, N. Letouze, University of Villetaneuse), the inter and intragranular elastic strain distributions have been investigated in a Dual-Phase Steel. This material exhibits an anisotropic elastic local behaviour and presents under load a heterogeneous strain (between the two different phases but also into a phase). “In situ” measurements, in the elastic range, have been realized adapting the loading machine of LMS. The measured Bragg peak displacements and their broadening allowed determining the mean strain of different crystalline orientations and the variance respectively. The data will be compared with a self-consistent estimation.
- A recent study concerning the microstrain investigation in single crystal nickel base superalloys exposed to thermal fatigue, has been performed in order to determine the strain state in gamma prime precipitates and in gamma matrix after different numbers of thermal cycles (J. Zrnik, P. Jencus, Slovakia; P. Lukas, Czech Republic).
- The accommodation of the intergranular strain incompatibilities caused by plastic deformation and/or thermal loading can lead to a field of heterogeneous elastic strain. Neutron diffraction experiments realized on the diffractometer "6T1", allowed to **analyse the residual elastic microdistortions for various crystallographic orientations** in a Zr alloy and to select the most precise theoretical model (N. Letouzé et al, LPMTM and SRMA) (see “***Highlight***”).

2. CRYSTALLOGRAPHIC TEXTURES

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. The understanding and the control of texture during the thermomechanical treatments or annealings are necessary to **optimise the material mechanical behaviour**.
Neutron diffraction is the best technique to determine the crystallographic texture of massive polycrystalline specimens (~ 1 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 mm^3) frequently met after primary or secondary recrystallization, for which the diffraction of conventional X-rays is not applicable. The LLB has dedicated the **6T1** 4-circles diffractometer to texture measurements. The texture studies are carried out usually in close collaboration with the “Laboratoire de Physicochimie de l’Etat Solide” (LPCES, Orsay University), where complementary techniques are performed: local texture and microstructure analyses by EBSD (Electron Back Scattering Diffraction) and by TEM (Transmission Electron Microscopy) as well as numerical simulations of the microstructure evolutions.

Recrystallization mechanisms and stored energy distribution

(M.H. Mathon, C.H. de Novion, LLB; T. Baudin, LPCES, Orsay University)

Within the framework of the **recrystallization mechanisms** study in various materials performed at the LLB in collaboration with the LPCES (Orsay), a method coupling the crystallographic texture and plastic microstrain analysis, both measured on the diffractometer "6T1", was developed. During a plastic deformation, part of the deformation energy is stored in the crystal lattice in the form of dislocations. This energy is one of the main driving forces of the recrystallization and its knowledge is very important for the understanding and the simulation of the texture evolution during the primary recrystallization.
The experimental procedure, based on the **Bragg peaks broadening analysis** measured for many crystallographic orientations describing a regular grid on the different {hkl} pole figures, allows to determine a **stored energy distribution function** and then to know the deformation energy stored by each crystallographic orientation. This kind of measurement was validated on the Fe-50%Ni alloy used in industry for its magnetic properties (transformers) and it was then extended to other materials (copper, duplex steel,...) and deformations (torsion,...).

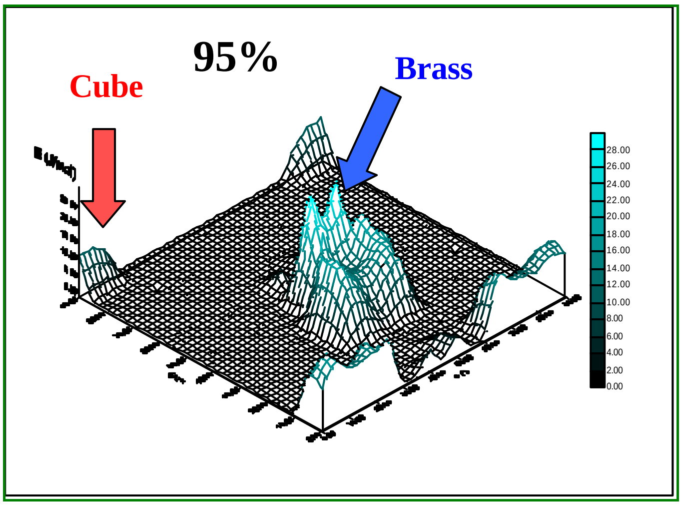

Figure 1. 3D view of the φ_2=0° section of the stored energy distribution function for the 95% cold-rolled Fe-50%Ni alloy. The stored energy is higher in the “Brass” ({110}<112>) orientation grains (around 18 J/mol) than in the “cube” ({100}<001>) orientation grains (around 8 J/mol).

In the **Fe-50%Ni alloy**, for a reduction ratio lower than approximately 60%, the primary recrystallization texture is similar to that of deformed specimens. For higher reduction ratios, it develops a strong "cube" component {100}<001>, the volume fraction of which is around 80% in the 95% cold rolled sample. The experimental determination of the stored deformation energy highlighted that the crystals presenting “cube” crystallographic preferential orientation store less energy than those presenting the rolling (“Brass” copper component) preferential orientations (see Figure 1). The difference increases with the rolling rate, furthering for the strong rates the growth of the "cube" orientation grains. In contrast, for the weak deformations, the variation of energy between the "cube" texture and the other components being insufficient, all the orientations can grow simultaneously and thus the texture tends towards an isotropic texture.

A large part of the crystallographic texture activity was focussed on the following studies: recrystallization mechanisms in various materials (FeNi, two-phase alloys, etc.), phase transformation effect on textures evolution in an industrial titanium alloy, correlations between crystallographic textures and thermomechanical history in geological materials (see the previous paragraph and the related "Highlight"). Let us quote, in particular, a fundamental study of the deformation and recrystallization mechanisms in an austeno-ferritic steel, undertaken in collaboration between the LPCES, the Institute of Metallurgy and Science of Materials of Krakow (Poland) and the LLB. The neutron diffraction experiments allowed to estimate successfully the stored energy levels in each phase according to the rolling reduction rate (0, 40 and 80%). The stored energy increases with the reduction rate and the values of stored energy appear larger for the γ-phase than for the α-phase. Concerning the ferrite, it is shown that the components inside the γ-fiber ({111} <uvw>) present a higher stored energy than the components included in the α-fiber ({hkl}<110 >). All these results are in good agreement with microstructural observations and stored energy evaluation (by calorimetry and TEM observations) performed on single-phase materials, especially ferritic steels.

Recrystallization mechanisms in industrial copper wires: “OPEFiC” project

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

Recently, the "textures" activity was marked, in 2001, by the start of "**OPEFiC**", a research project partly subsidized by the French Research Ministry, including three laboratories (LLB, LPCES, LPMTM of Villetaneuse University) and two 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 understanding of the various metallurgical phenomena inherent in the continuous casting and rolling processes should allow an optimisation of manufacture conditions and of the choice of the raw material according to the final wire use.

3. STUDY OF PHASE TRANSITIONS, HETEROGENEITIES, PRECIPITATION AND AGEING

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” (Nancy University) concerning the ageing of Pb-Ca-Sn alloys used in the Pb accumulators, and with the Ecole des Mines (Albi) on the effect of a heat treatment and of cyclic plasticity on the precipitation sequence in a steel. Let us quote also the work of the Austrian CRG team on the 3-axis machine G4.3 that is detailed at the end of this paragraph.

Ageing behaviour of martensitic materials under irradiation

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

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**. The nuclear reactor constitutive materials, exposed to a neutron flux and/or to high temperatures for very long durations, can present, with increasing time, a progressive degradation of their dimensional or mechanical properties related to a microstructural evolution (swelling, embrittlement due to a new precipitated phase, irradiation-induced specific defect clusters...). It is then necessary to control these microstructural evolutions to be able to **predict the in-service behaviour** of the materials. In this context, SANS presents often advantageous contrasts between the matrix and the precipitates. Moreover, for ferromagnetic materials, additional information about the precipitate chemical composition is extracted from the magnetic scattering.
Recent SANS studies at the LLB were focused on **martensitic materials** which are candidates for the internal structure of future generation reactors (such as fusion or advanced high temperatures reactors) or

spallation sources, because of their remarkable resistance to swelling and their adequate mechanical properties at relatively high temperatures. These include conventional commercial 7-12% Cr steels, reduced activation materials and oxide reinforced materials (ODS).

Conventional and Reduced Activation Martensitic steels have been the subjects of a detailed work for several years. This work allowed to precise the conditions and the **kinetics under irradiation of the phase separation** of the ferrite into two isomorphous body centred cubic (b.c.c.) phases, one Fe-rich (α phase) and the other Cr-rich (α' phase), which is partly responsible for **hardening** and **embrittlement** of the material at relatively low temperature (< 400°C) and moderate dose (≈ 1 displacement per atom (dpa)) (see "Highlight").

The 9Cr-1Mo martensitic steels are candidate materials for the spallation sources. In these materials, the formation of a significant quantity of helium can induce a degradation of the mechanical properties. The helium effect has been studied in EM10 and T91 commercial martensitic steel samples implanted with 0.5 at% helium. The microstructural analysis was performed by TEM and SANS. **Helium bubbles** were detected in both materials implanted at 250 and 550°C and bubble size distributions as well as number densities were determined. Furthermore, the SANS experiments showed that these bubbles are close to thermodynamic equilibrium, i.e. their internal gas pressure is balanced by the surface tension. Based on the microstructural results, it is shown that the high degree of hardening of specimens implanted at 250°C is due to the high density of tiny helium bubbles.

The materials reinforced by oxides dispersion, usually called **ODS (Oxide Dispersion Strengthened)**, have a vast applicability because of their excellent mechanical resistance at medium and high temperatures. They are elaborated by mechanical alloying starting from the components in the form of elementary or alloyed powders. Within the framework of nuclear applications, ODS-based Fe alloys are considered within the international community as potential candidates for any structure subjected to high neutron damage at high temperature (400-700°C) and under constraint. Indeed, the b.c.c. structure of ferrite ensures material a resistance to swelling under irradiation, and the dispersion of oxides improves the mechanical properties (creep, ….) at high temperatures. SANS experiments allow to characterize finely the nanometric oxides distribution in the matrix at various stages of the development process, but also after thermal ageing and under irradiation. In this work, several Fe-9Cr ODS martensitic steels were characterised. It has been shown that the austenite <=> ferrite /martensite phase transformation has no effect on the size distribution of the oxides (Y_2O_3) when the material is cycled in temperature. On the other hand, neutron irradiation at 325°C does not induce any modification of the oxides population up to 5.3 dpa, but involves the formation of chromium-rich b.c.c. α' precipitates in the ferritic matrix (see figure 2).

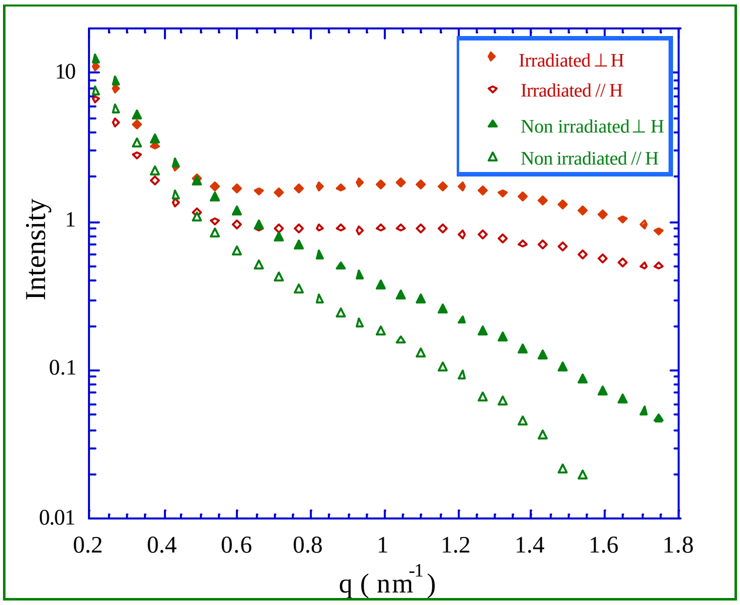

Figure 2. Scattered intensity measured perpendicular and parallel to the applied magnetic field on a non-irradiated and an irradiated (2 dpa at 325°C) ODS martensitic alloy.

Helium damage in long aged metal-tritium systems: Ta, Y and Sc

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Helium damage due to tritium decay in metals is considered as one of the major technical challenges in the construction of future fusion reactors ("first-wall problem"). Continuous helium production induces complex defect structures due to helium clustering and bubble formation with increasing helium content. Earlier studies on bcc Ta were continued and complemented by investigations on hcp yttrium and scandium. Polycrystalline samples of tantalum, yttrium and scandium were loaded with tritium concentrations of about ten atomic percent and the evolution of several Debye-Scherrer lines with respect to position, shape and intensity was investigated repeatedly over a time range covering 10-15 years. These high-resolution measurements were done on the triple axis spectrometer G43 (VALSE). Changes in the line shapes with increasing helium content can be interpreted in terms of a steadily growing number of induced lattice defects: The produced helium atoms cluster and form bubbles entailing increasingly strong lattice strains which finally give rise to the formation of dislocation loops in the host lattice. At later stages an interconnected dislocation network develops which broadens the Debye-Scherrer lines. Tritium on interstitial sites expands the host lattice thus leading to shifts in the lattice parameter. The lattice damage is strongly anisotropic in the hexagonal systems (Y-T and Sc-T) and reflects their elastic properties. A somewhat different behaviour was observed in an yttrium sample cooled to liquid nitrogen temperature immediately after the charging process and kept at this temperature over several years.

Martensitic phase transitions in pure Lithium

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The martensitic phase transformation of Li at low temperature is characterized by a complicated phase diagram exhibiting a coexistence of several close-packed phases with the bcc matrix, large thermal hystereses and a number of precursor phenomena. At 80K a rhombrohedral 9R phase (space group R3m) is formed on cooling. On heating, it transforms into an fcc structure at about 100 to 120K while the fcc-bcc reverse transformation occurs only at about 180K. Experimental and theoretical work by the investigators indicates that, contrary to common belief, fcc is the true equilibrium phase of Li at low temperatures and that the 9R phase is only formed as a consequence of geometrical constraints that inhibit direct nucleation of fcc from bcc.

The orientational relationships between bcc matrix and several variants of the 9R phase were investigated in partly transformed Li single crystals on the spectrometer G4.3. Perfect agreement between calculations based on the crystallographic theory of martensite and the experiment was found within the resolution of the instrument. After the formation of the fcc phase the evolution of both the fcc and 9R phase was studied in thermal cycling experiments between 5K and 120K on heating and cooling.

In a small-angle scattering experiment on G5.4 the formation of martensite nuclei induced by small uniaxial deformations in the undercooled bcc phase of Li was investigated. A special deformation cryostat was constructed which allows well-controlled uniaxial in-situ compression and mounting of the oxidation-sensitive Li crystals in a glovebox under protective atmosphere. A uniaxial compression of 3% at 120K leads to two anisotropic peaks in the scattering pattern showing the presence of particles whose size is in the range of 25Å and which are distributed in the (001) plane normal to the compression axis. The scattering pattern remains stable over a wide temperature range even on heating and is indicative of the formation of small martensite embryos which may explain anomalies observed, e.g. in mechanical properties and diffusion experiments well above the transition temperature.