ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

C. R. Physique 8 (2007) 789–805

COMPTES RENDUS

PHYSIQUE

http://france.elsevier.com/direct/COMREN/

Neutron scattering/Diffusion de neutrons

A review of in situ and/or time resolved neutron scattering

Olivier Isnard [a,b,c,*]

[a] *Institut Néel, CNRS, Boîte F, BP 166, associé à l'Université J. Fourier, 38042 Grenoble cedex 9, France*
[b] *Institut Universitaire de France, Maison des Universités, 103, Boulevard Saint Michel, 75005 Paris cedex, France*
[c] *Institut Laue–Langevin, 6 rue J. Horowitz, BP156, 38042 Grenoble cedex 9, France*

Abstract

Thanks to the ability of neutrons to penetrate deep into matter, experiments can be performed in situ in real conditions. The development of dedicated instruments on high flux neutron sources also enables fast data acquisition. As a consequence, it is now possible to investigate not only in situ but also time resolved physical or chemical processes over several time scales ranging from hours to a few milliseconds. Several recent examples are taken in different fields of research: physics, magnetism, chemistry, metallurgy, electrochemistry, polymers and archeometry. Among the scattering techniques that can be used to perform in situ or time resolved experiments we present results of powder neutron diffraction, small angle neutron scattering, and neutron radiography. ***To cite this article: O. Isnard, C. R. Physique 8 (2007).***

Résumé

Une revue sur la diffusion des neutrons réalisée in situ et/ou résolue en temps. La forte pénétration des neutrons dans la matière permet d'effectuer des expériences in situ, dans des conditions réelles. Sur les sources à haut flux de neutrons, le développement d'instruments spécialisés, dédiés à ces études, rend possible des acquisitions très rapides. Ainsi, il est désormais possible d'effectuer non seulement des études in situ mais aussi résolues en temps afin d'étudier des processus physique ou chimique sur plusieurs échelles de temps s'étalant de quelques millisecondes à l'heure. De nombreux exemples récents seront présentés, pris dans divers domaines de recherche : physique, chimie, métallurgie, magnétisme, électrochimie, polymères et archéologie. Parmi le large éventail de techniques neutroniques qui peuvent être effectuées in situ ou en temps réels, nous présenterons ici des résultats de diffraction neutronique sur poudre, de diffusion des neutrons aux petits angles et de radiographie neutronique. ***Pour citer cet article : O. Isnard, C. R. Physique 8 (2007).***

Keywords: In situ studies; Powder neutron diffraction; Time resolved investigation; Small angle neutron scattering

Mots-clés : Études in situ ; Diffraction neutronique sur poudre ; Expériences en temps réels ; Diffusion des neutrons aux petits angles

---

1. Introduction

Several articles have been devoted in the past to in situ neutron diffraction studies, among which one can cite [1–6]. The recent years have been the occasion for numerous technical developments of both the neutron sources,

---

[*] Correspondence to: Institut Néel, CNRS, Boîte F, BP 166, associé à l'Université J. Fourier, 38042 Grenoble cedex 9, France.
E-mail address: Olivier.Isnard@grenoble.cnrs.fr.

1631-0705/$ – see front matter © 2007 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.
doi:10.1016/j.crhy.2007.10.002

with the increasing performance of the spallation sources, and of the neutron scattering instruments. Several neutron scattering techniques are now available for scientists and engineers to perform in situ studies and (or) time resolved investigations. These experimental advances have significantly widened the field of research that can be undertaken by neutron scattering techniques. To illustrate the potential of neutrons we will present here examples of in situ studies taken from different fields of research.

It is probably worth defining what is meant by 'in situ' neutron studies. This term will be used by the author to refer to experiments performed in real conditions, such as at high temperature, in reaction cells or in a controlled gas atmosphere. This term can also be used to refer to non-destructive studies. The usefulness of non-destructive neutron diffraction to probe in situ the residual stresses of bulk materials and components is outside the scope of the present article but is treated extensively in the article of P.J. Withers [7] in the same volume. The term in situ is also often used to define studies performed in real time during synthesis itself, thus enabling the demonstration of the presence of transitory phases which may disappear at the end of the process. Two examples of such studies are given in Section 2. The use of neutron diffraction measurements, first to probe the crystallisation of amorphous materials by thermodiffractometry, and second to investigate the mechanism of formation and ordering of alloys, will be described. Numerous chemical processes can be investigated in situ, in order to have a better knowledge of the reaction mechanisms and to show the different states of the processes. Among these, Section 3 will highlight the case of a solid–gas reaction during the insertion and/or desorption process of interstitial atoms, as well as the oxidation reaction. In Section 4 we present some examples of neutron scattering in the field of energy storage and batteries. Indeed, the use of batteries and the growing demand for portable power sources focuses research onto electrochemical devices containing light element like H, Li, ... or fuel cells using anionic and cationic mobility. Neutrons are thus the ideal probe to investigate newly discovered materials presenting possible potential for applications, or else to improve existing technologies by analysing the mechanisms involved.

In order to illustrate the usefulness of in situ Small Angle Neutron Scattering (SANS) to determine the structure at several nanometers scale, two examples are described in Section 5: (1) the study of the precipitation and growth of hardening precipitates in Ni based superalloys; and (2) the study of the structure of phase transitions in liquid-crystal polymers.

Non-destructive neutron techniques are presented in the following two sections. Section 6 deals with examples of neutron radiography studies, and Section 7 describes the impact of neutron scattering techniques in archeometry. The last section is devoted to time resolved investigations highlighting the efficiency of SANS and powder neutron diffraction to investigate fast kinetic processes. The limits of the neutron scattering techniques, in particular the time scales accessible, will be given, commented on, and compared to those accessible nowadays by in situ X-ray diffraction.

Finally, it is worth mentioning that the examples described below have been chosen among the extensive literature on the domain, but all applications of neutron scattering are not covered here. In particular, due to the ability of neutrons to penetrate deep into complex sample environments, neutron scattering has been widely used for many years to investigate structural or magnetic phase transitions. These studies, which are now classically performed versus temperature, pressure, magnetic field or strains, are not discussed below. Examples of such magnetic structure investigations can be found in the references [3,5,8–11].

2. Thermodiffractometry

2.1. Crystallisation of amorphous materials

Whereas diffraction is mainly used to probe crystalline materials it can also be used to investigate amorphous materials. Indeed, as can be seen from Fig. 1, recording the in situ diffraction pattern of an amorphous material (Zr–Ti–Cu–Ni alloy) heated in a furnace enables one to show the different steps of crystallisation. This is particularly important in the field of bulk metallic glasses whose exceptional mechanical properties are directly related to their amorphous state [12,13]. It is thus of prime importance to know their range of existence in the amorphous state. The use of neutron diffraction permits us to probe deep inside the synthesised alloy and to show that the material does not contain any crystalline phase. On heating, the alloy transforms irreversibly to transient or stable phases. Several steps are demonstrated in the diffraction pattern, steps which can be correlated to the anomalies observed by differential scanning calorimetry (DSC). Such a DSC signal is shown in the insert in Fig. 1. Nevertheless, some evolution, such

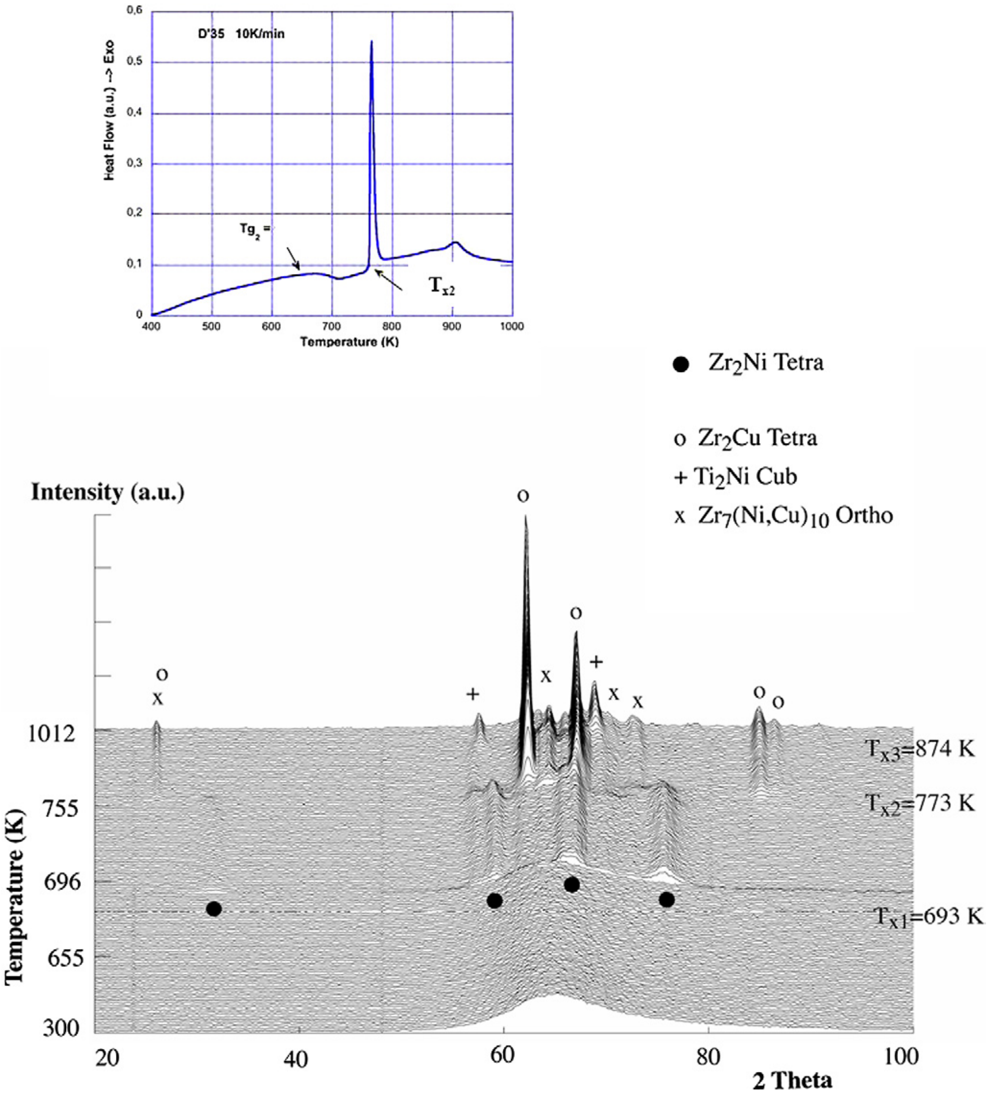


Fig. 1. Thermal evolution of the neutron powder diffraction pattern upon heating an amorphous alloy of Zr–Ti–Cu–Ni type [12,13]. Insert: Differential scanning calorimetry signal recorded on the same sample.

as the crystallisation of the tetragonal form of Zr_2Ni, can barely be seen in the calorimetric measurement, but is more easily shown by neutron diffraction. Even for the large DSC signal observed at temperatures larger than 740 K, the analysis of the neutron diffraction pattern provides additional information, such as the nature of the crystalline phases obtained, and the temperature at which the crystalline grains are large enough to give rise to significant Bragg intensity. Neutron diffraction measurements show that the amount of Zr_2Ni decreases, while new crystalline phases of Zr_2Cu (tetragonal), Ti_2Ni (cubic) and finally $Zr_7(NiCu)_{10}$ appear.

This type of investigation can now be widely performed to study the crystallisation products from amorphous materials [14]. It has also been applied to follow the formation of metastable icosahedral phases from metallic glasses [15]. However, more generally, thermodiffractometry, that is to say the investigation of the thermal dependence of the diffraction pattern, can provide useful information to study the crystal structure distortion or to investigate chemical processes, for example, the Jahn–Teller distortion occurring in $NaNiO_2$ has been followed by thermodiffractometry [16]. In a completely different field, the hydration of cement can be studied in situ using neutron diffraction. Examples of such studies can be found in Refs. [17–19].

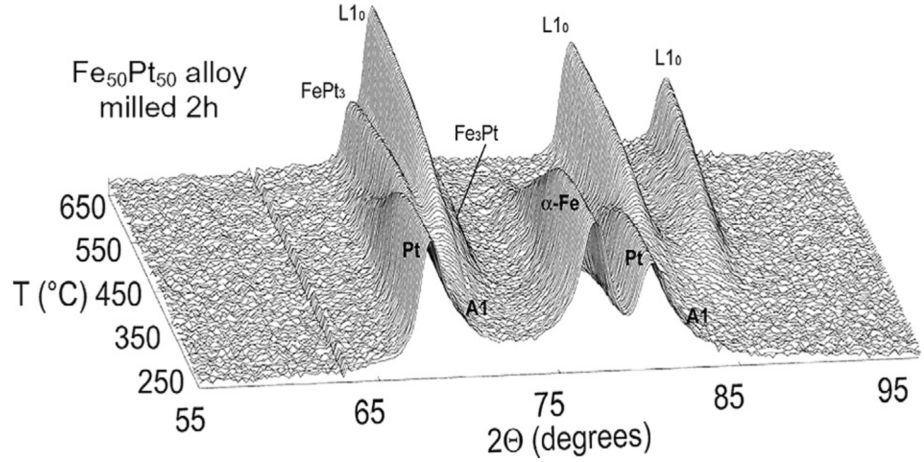


Fig. 2. Thermal evolution of the neutron diffraction pattern of Fe50Pt50 nanocrystalline alloy made from a Fe (cc) + Pt (fcc) mixture milled two hours at 77 K. The diffraction pattern has been recorded upon heating in situ during the ordering of the alloys into the $L1_0$ phase. The diffraction peaks corresponding to the phases observed are indicated [20].

2.2. *Formation and ordering of alloys*

A recent example of thermodiffractometry is the ordering of nanocrystalline Fe–Pt alloys [20]. The FePt alloys have attracted considerable attention during the last few years since they are considered as candidates for ultrahigh-density magnetic storage media and as materials for special permanent magnet applications. The excellent magnetic properties of these alloys are associated with the tetragonal $L1_0$ FePt phase formed from the face-centred cubic disordered A1 phase by ordering Fe and Pt atoms. Both experimental data and theoretical calculations have indicated a correlation between the degree of order within the $L1_0$ phase and the magnetic properties, such as magnetocrystalline anisotropy and Curie temperature. Fig. 2 presents the thermal evolution of the neutron diffraction pattern for $Fe_{0.5}Pt_{0.5}$ powders obtained by mechanical alloying after 2 h of milling. The in situ investigation [20] has shown the coexistence of several phases during thermal treatment: other off-stoichiometric phases such as Fe_3Pt and $FePt_3$ have been found to appear as well. The Rietveld analysis of all the recorded diffraction patterns allows the quantitative determination of the volume fraction of each phase, as well as its temperature variation [20]. The comparison of the diffraction pattern recorded for different milling conditions [20,21] is thus very useful to both better understand and optimise the ordering process and the magnetic properties. The reader is referred to Figs. 3 to 7 of Ref. [20] for more details. Furthermore, while cooling down an ordered $L1_0$ phase and recording the thermal evolution of the neutron diffraction pattern, one can follow the progressive magnetic ordering and quantify the magnetic moments [21]. Further examples of magnetic studies can be found elsewhere [8–11,22–24].

In situ thermodiffractometry neutron diffraction experiments are not restricted to neutron research reactors and are already widely accessible on spallation neutron sources where dedicated instruments have been developed during the last few years [25,26]. Investigations of the crystallisation of amorphous alloys have been undertaken in other systems [27,28] and many other thermodiffraction studies are now possible on spallation sources [29]. The structure of the amorphous or disordered materials can be investigated there too [26,30].

3. In situ studies of solid–gas reactions

3.1. *Study of the insertion and/or desorption of interstitial atoms in the structure*

Various chemical processes can be investigated in situ, in order to have a better knowledge of the reaction mechanisms and to show the different stages of the processes. In this section we will give a few examples of solid–gas reactions as studied by powder neutron diffraction.

It has been found to be possible to insert interstitial atoms like H, C or N in the crystal lattice of the R_2Fe_{17} phases (R being a rare-earth element) [31–33]. The presence of these interstitial elements induces a tremendous change of the

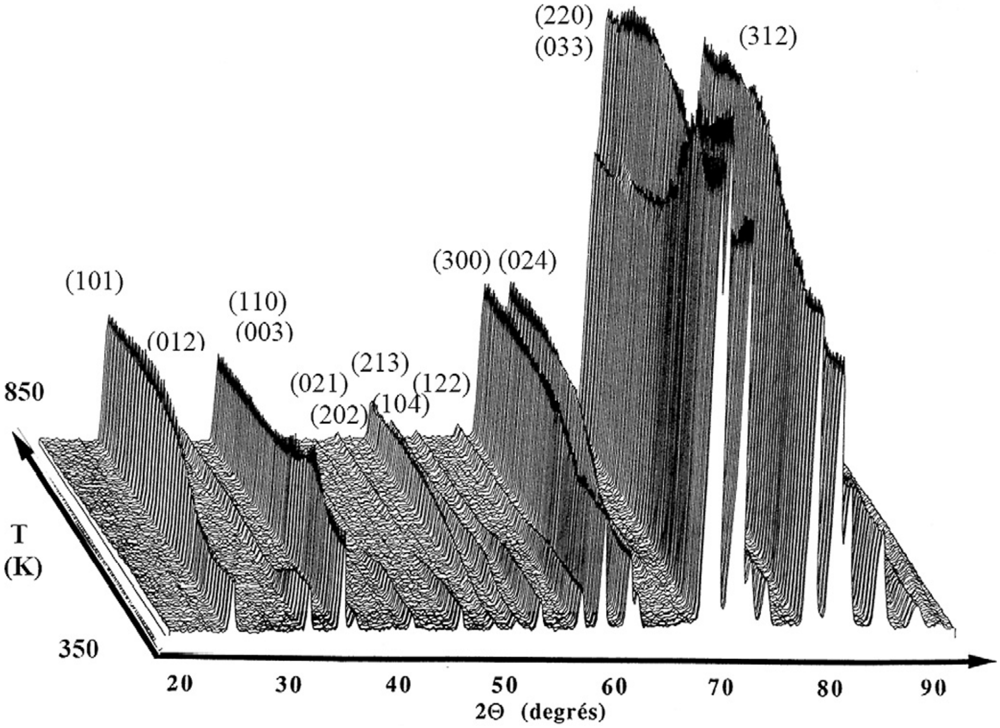


Fig. 3. Evolution of the powder diffraction pattern of $Nd_2Fe_{17}D_5$ upon desorption of deuterium from the Nd_2Fe_{17} phase [34].

magnetic properties, so that the phases containing interstitial atoms exhibit hard magnetic properties and that some of these phases are used in high performance permanent magnet applications. In the case of hydrogen inserted in Nd_2Fe_{17}, two non-equivalent interstitial sites have been found to accommodate H atoms in the crystal structure: an octahedral site and a tetrahedral site, referred to as D_1 and D_2 respectively [31,34]. The hydrogen insertion occurs via a solid–gas reaction between the H_2 gas and the intermetallic Nd_2Fe_{17} phase. This insertion is fully reversible, since heating $Nd_2Fe_{17}H_5$ under dynamic vacuum promotes hydrogen release. The corresponding evolution of the neutron diffraction pattern during the desorption process is shown in Fig. 3 [34]. The intensity of the Bragg peak evolves upon heating. The shift of the Bragg peak position is a result of the contraction of the unit cell occurring when hydrogen atoms leave the crystal structure. A Rietveld refinement of each diffraction pattern recorded upon heating has led to the results presented in Fig. 4. It is clear that hydrogen leaves the tetrahedral D_2 site first, between temperatures T_1 and T_3, whereas the D_1 site keeps its hydrogen content to its maximum of three H atoms per formula unit up to about 500 K [34,35]. Above this temperature, the hydrogen release occurs on the octahedral site, a desorption that ends at ca. 700 K. Such in situ neutron diffraction analysis clearly proves the higher thermal stability of the octahedral site compared with the tetrahedral one. This has been linked to the local atomic environments of the H atoms on both sites [34,35] and to the larger volume of the D_1 interstitial site.

In addition to the determination of the crystal structure and the study of its temperature dependence, neutron scattering can provide much more information, in particular concerning the dynamics of the interstitial atoms. The huge incoherent neutron scattering cross-section of H compared to any other atom, is thus an advantage to probe its dynamics in the structure. Such investigations have been performed on isotype Pr_2Fe_{17} based hydrides by quasielastic neutron scattering as well as neutron vibrational spectroscopy; examples of which can be found elsewhere [36,37]. On the basis of both the frequency and the intensity of the inelastic peaks, these investigations have confirmed the interpretation of the in situ neutron diffraction results, in particular the lower stability of the tetrahedral site versus the octahedral one. In the R_2Fe_{17} phases, insertion of other interstitial elements such as C or N has been studied in situ. For more information the reader is referred to the following articles [33,38,39].

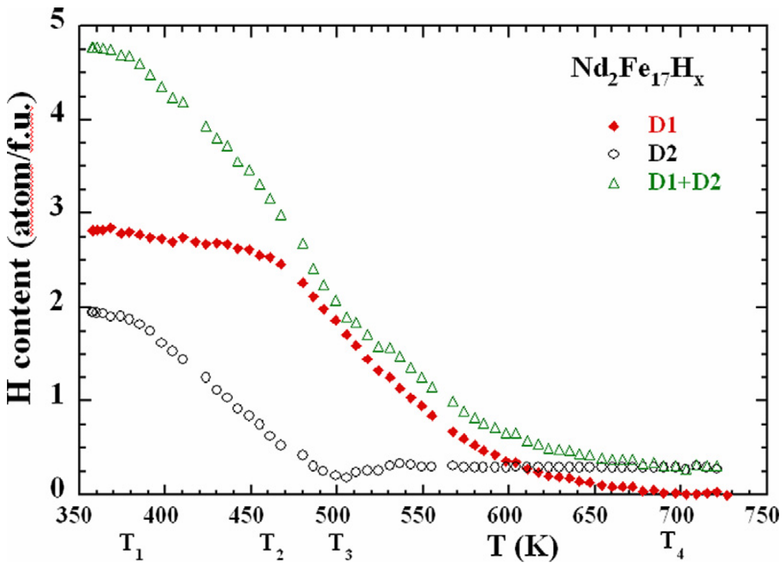


Fig. 4. Evolution of the interstitial site occupancy deduced from the refinement of the neutron diffraction patterns recorded upon hydrogen desorption from the $Nd_2Fe_{17}H_x$ crystal structure [34]. D1 and D2 refer to two non-equivalent interstitial sites occupied by hydrogen.

3.2. In situ studies of oxidation reactions

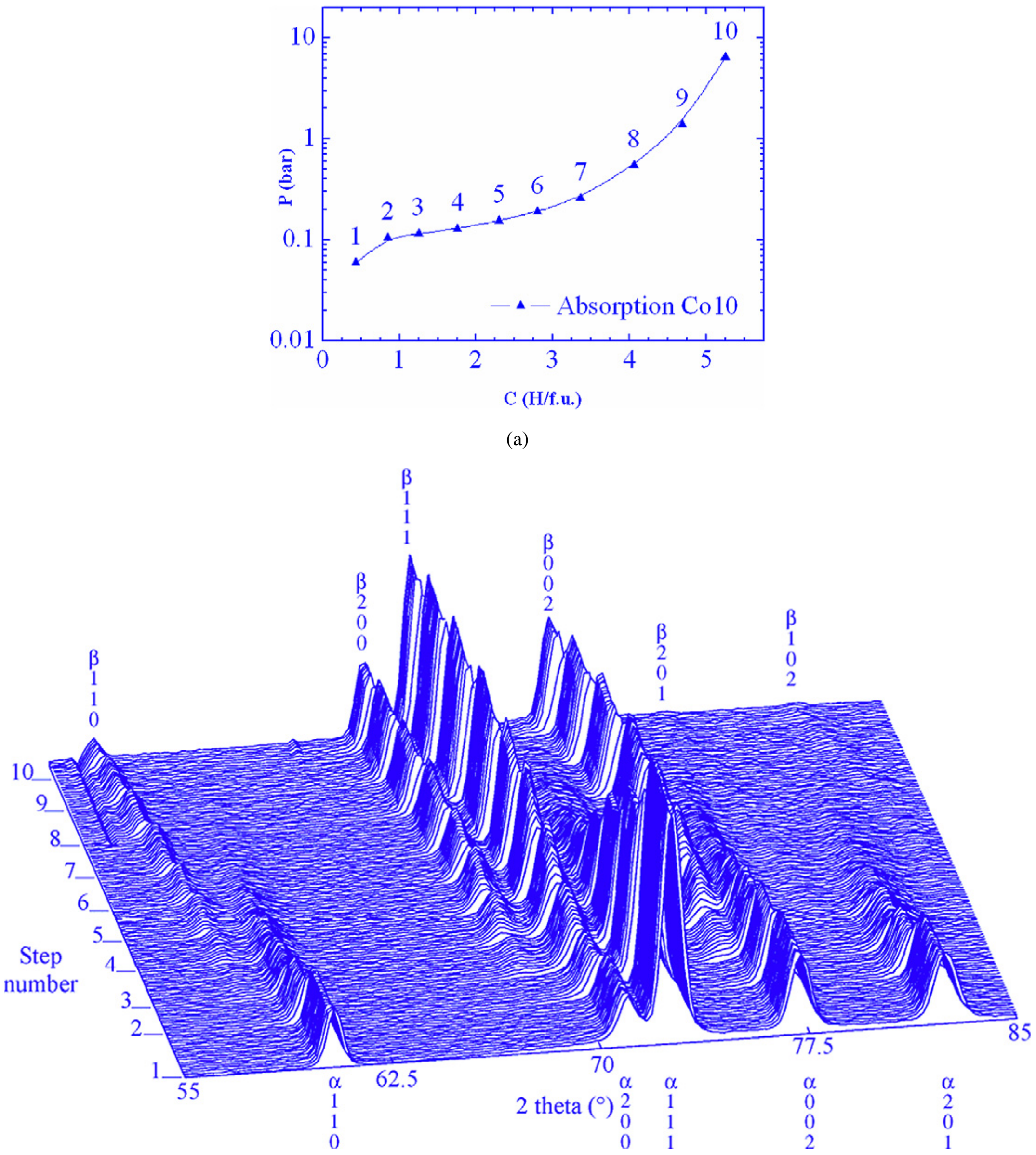
Oxide compounds are also often studied by neutron diffraction, since oxygen can be more precisely located by this technique than with conventional X-ray or electron diffraction. The in situ neutron diffraction study can also be very useful to determine simultaneously the stoichiometry and the atomic positions of oxygen during synthesis. An example is the case of the over-stoichiometry in the Ce pyrochlore compound. Indeed, it has been shown that the recently synthesized $Ce_2Sn_2O_7$ is able to fix one oxygen leading to the formulation $Ce_2Sn_2O_8$ [40]. The pyrochlore symmetry was found to be conserved but two original complex defects have been found: the first one close to the Ce atoms, associating an oxygen vacancy with four interstitial oxygens, the second, close to the Sn atoms, increasing to seven its coordination number.

Many neutron scattering experiments have been devoted to the study of the superconducting cuprates. A study of the oxidation of $YBa_2Cu_3O_6$ into $YBa_2Cu_3O_7$ has been performed in situ by neutron diffraction [41]. This has permitted one to follow the tetragonal–orthorhombic distortion occurring during the chemical reaction with the oxygen gas. The oxygen content and its location in the crystal structures have been determined at each step of the solid–gas reaction.

4. In situ studies of chemical processes in the electrodes of batteries

The field of energy storage benefits considerably from neutron scattering techniques. We will present below a few selected applications of neutron scattering in this field and give references to other examples.

Intermetallic compounds are able to reversibly store hydrogen near room temperature and ambient pressure. Storage is achieved electrochemically by reduction of water or chemically by hydrogen gas dissociation. $LaNi_5$-type alloys are used as Ni-MH negative electrode materials. La and Ni substitutions lead to competitive compounds with complex formula $Mm(Ni_{4.3-x}Mn_{0.4}Al_{0.3}Co_x)_{1+y}$ where Mm stands for mishmetal, a cheap mixture of rare-earths. On neutron diffraction patterns recorded during the hydrogen insertion, three structural domains can be observed (Fig. 5(a)): at low H content, a single phase solid solution domain (so-called α-phase) occurs in the $LaNi_5$ structure. This region is followed by a two-phase domain, where the saturated α-phase transforms into the high hydrogen containing β-phase described in Fig. 6. It corresponds to a constant plateau pressure that extends in composition as long as the transformation reaction takes place. These different domains can be characterised during in situ neutron diffraction experiments. As shown in Fig. 5(a), the multi-substituted $LaNi_5$-type compound $Mm(Ni_{0.712}Mn_{0.076}Al_{0.058}Co_{0.15})_5$ is loaded in situ (in the pressure cell) under hydrogen pressure by a controlled step-by-step process up to a tenth of a bar. At each step, the sample is allowed to relax until it reaches equilibrium [42]. Simultaneously, a thermodynamic



(a)

(b)

Fig. 5. (a) Central part of the powder diffraction pattern recorded upon charging hydrogen in the LaNi$_5$-type compound at room temperature. The phase type (α and β) are indicated close to the Bragg peaks together with the *hkl* values [42]. (b) Pressure Composition Isotherm (PCI) curves at 25 °C for the Co 10 wt% Mm(Ni$_{0.712}$Mn$_{0.076}$Al$_{0.058}$Co$_{0.15}$)$_5$ alloy obtained during the in situ neutron diffraction experiment [42].

characterization of the intermetallic–hydrogen system is carried out by recording the pressure-composition isothermal (PCI)—Fig. 5(b). Indeed, the stability of the hydride formed is determined by its hydrogen equilibrium pressure at a given temperature [43,44]

Step numbers given in Fig. 5(a) correspond to the equilibrium states shown on the PCI curve (Fig. 5(b) left). Absorption occurs in three different sequences:

(i) α solid solution branch from steps 1 to 3,
(ii) α–β two-phase domain (on plateau pressure) from steps 3 to 7,
(iii) β solid solution branch from steps 7 to 10.

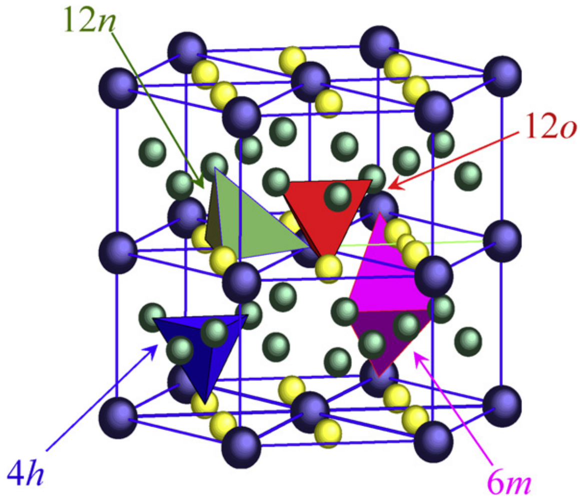


Fig. 6. Crystal structure of the $LaNi_5H_x$ type compound showing the tetrahedral interstitial sites occupied by hydrogen atoms in the β-phase. The big and small balls refer to the La and Ni atoms, respectively.

The combined and simultaneous measurement of thermodynamic properties and structural information by in situ neutron diffraction enables one to have a deeper understanding of the metal hydride behaviour. Indeed, at each step, the H content can be quantified, and its location in the crystal structure determined. The percentage of each phase has been quantified and the inserted atoms have been located on four different interstitial sites, which are shown on Fig. 6.

It has been shown that, at equivalent charge, that is to say for the same hydrogen content, different behaviour occurs for solid–gas absorption and for electrochemical charge. Consequently, in situ studies using powder neutron diffraction have been performed on working negative electrode materials. This technique is very powerful since it allows a bulk analysis of the electrode in a configuration very close to real batteries. During the measurements, the electrochemical charge or discharge process is monitored by the current density imposed by a galvanostat. The electrochemical properties are recorded simultaneously with neutron diffraction pattern, thus enabling us to combine all the information during the analysis. Using real time experiments, different possible negative electrode materials with various weight ratios of Co have been investigated. For Co-rich alloys containing mishmetal, the existence of the intermediate γ-phase has been shown [45,46] (see Fig. 7). This phase has a cell volume and hydrogen storing capacity intermediate to those of the α- and the β-phases. It plays a very important role in the strain distribution within the grain. The crystal structure of the γ-phase, described elsewhere [46,47], is similar to that of the β-phase but with a lower occupancy of the interstitial sites.

An interesting feature is related to volume expansion and reduction during the operation of the electrodes. Indeed, an intermediate hydride implies a two-step process in the discrete volume expansion (α–γ, γ–β) allowing the system to reduce the strains generated at the α–β interface and, therefore, limiting the decrepitation process and minimising the subsequent corrosion. This corrosion in the highly alkaline electrolyte is a problem, since it is known to reduce the useful number of cycles during the lifetime of the NiMH batteries [46–48]. It can be overcome by substituting cobalt on the nickel site of the intermetallic compound. The benefit brought by this element is connected with the formation of an intermediate γ-hydride mentioned earlier. More generally, the presence of the γ-phase depends not only on the alloy composition, but also on the formation process (only during electrochemical charge) [47].

Details of the electrochemical cell specially developed for such in situ investigations can be found in Refs. [3,45,49]. This approach has been also successfully applied to probe the nickel oxyhydroxide electrodes, which constitute the other electrodes of these Ni-MH rechargeable batteries. The redox processes have been investigated in situ by neutron diffraction on protonated or deuterated electrodes [49]. Both the γ- and β-NiOOH phases are found to transform directly and continuously to the β-$Ni(OH)_2$ phase upon reduction. This has allowed one to show that the so-called second plateau phenomenon occasionally occurring during the electrochemical reduction is not due to any intrinsic structural property of the active material but is related to its surface properties, being prone to be strongly dependent on the electrode preparation.

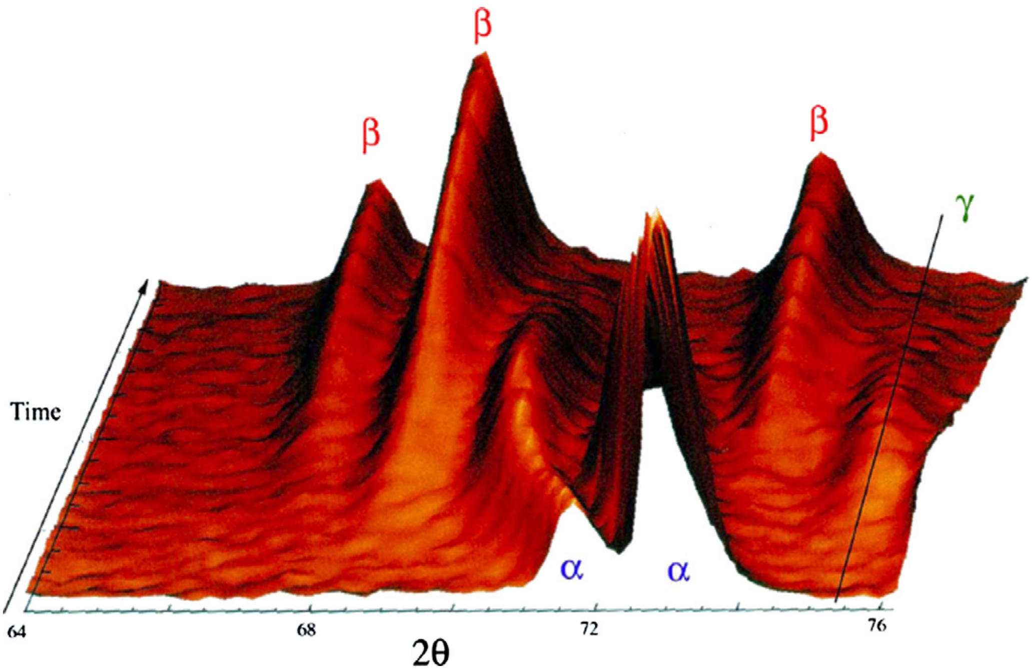


Fig. 7. Three-dimensional view between 64 and 76° (2Θ) of the diffraction patterns during the charge of the working electrode. The charge duration was about 15 hours. One can note the appearance and disappearance of a peak belonging to the γ-phase at $2\Theta = 75.5°$ on the right of the plot [46].

Similarly, other complex electrochemical systems such as the H/γ-MnO_2 system, have also been studied in situ during the operation of the electrode [50–52].

The ionic conductors are also an important class of materials that can easily be probed by neutron scattering. In addition to the ionic mobility, which can be analyzed by inelastic or quasielastic neutron scattering, their structure can be investigated by diffraction [53]. An illustration is the BIMEVOX materials that derive from the parent compound $Bi_4V_2O_{11}$ by partial substitution of a metal for vanadium. They exhibit high oxygen ion conduction at moderate temperatures, 300–700 °C, and could find applications as membranes for oxygen separation. An in situ and time resolved neutron diffraction experiment was performed under electrical bias on $Bi_4V_2O_{11}$ and BICOVOX membranes in order to analyse the electrochemical reduction of these electrolytes at the cathode under working conditions [54]. The experiments were carried out at 620 °C, under an air atmosphere. Under cathodic polarisation, the bi-dimensional structure of the BIMEVOX compound is retained and the observed changes in unit-cell parameters are due to a slight variation in oxygen stoichiometry which is easily recovered when the current is turned off and the membrane reheated at higher temperature. This confirms the reversibility of the process.

5. In situ small angle neutron scattering

While neutron diffraction is one of the most used techniques, in situ studies can also be performed by other methods such as small angle neutron scattering (SANS) and neutron radiography (see next section). Indeed, investigation by SANS can reveal inhomogeneities inside materials of typical size ranging from 1 nm to 50 nm, and determine their shape and size [55,56]. Typical examples of such studies are the investigation of (i) phase separation in binary or ternary systems or (ii) fluctuations of density and concentration in single phase systems or solutions [57,58]. This has been done in metallurgy, but also in the field of polymers [59,60].

For example: nickel-based superalloys are of great industrial interest, particularly for turbine blades in aeronautics. Their microstructure consists of two phases: cuboids of a long range ordered γ'-hardening phase and an fcc γ-matrix. Such complex alloys can be studied in situ by small angle neutron scattering to follow the coalescence and the precipitation of the γ'-phase with temperature. These studies have shown the importance of the cooling rate on the shape and size of the precipitates. Slow cooling rate favours spherical precipitates whereas fast cooling promotes the formation of square shaped precipitates [61,62]. The kinetics of the strain induced directional coarsening have also been studied

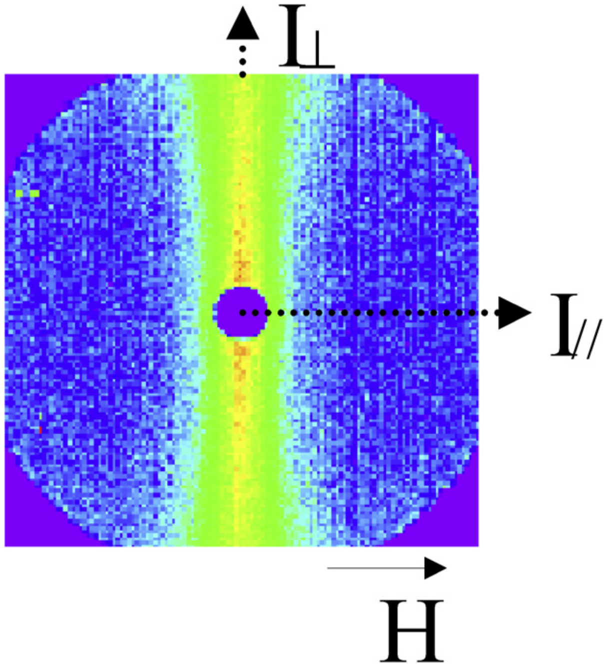


Fig. 8. Small angle neutron scattering pattern recorded from a liquid crystal in the nematic phase, under an applied magnetic field [67,68]. The red and blue colours correspond to the highest and lowest scattered intensity respectively. The observed pattern is the Fourier transform of the scattering object.

in a furnace under an applied stress [62] (in situ on SANS instruments like D11 at ILL). In these experiments one can access the time as well as the thermal dependence of such processes. Complementary investigations have been undertaken by in situ neutron diffraction at LLB-Saclay [63], where the fraction of γ'-phase in the superalloy has been quantified in a non-destructive manner between 20 and 1300 °C. It is worth noting that other techniques, such as elastic diffuse neutron scattering, have also been used to probe the local order in the γ-phase of superalloys [64].

Polymers are another research field which benefits a lot from small angle neutron scattering techniques. Neutron scattering presents two main advantages versus X-rays: a larger sensitivity to light atoms (like H, C, ...) and the possibility to play with the selective isotopic substitution of H by D atoms to enhance the contrast between molecules or solvents. Using small angle neutron scattering, the polymer main chain deformation under shear has been studied in situ (in dedicated shear cells). This has led to the observation of shear induced phase transitions such as nematic-isotropic transition in liquid-crystal polymers [65] or other transitions [66]. Several studies have been undertaken in situ under an applied magnetic field in order to determine the conformation of main chain liquid-crystal polymers in bulk [67,68]. The conformation of main chain polyester has thus been determined to be Gaussian in the isotropic phase. In the nematic phase, the SANS data have been fitted by a model of cylinder in which the main chain polymer is confined. The radius-to-length ratio of the cylinder can be deduced from the SANS pattern given in Fig. 8. Under an applied magnetic field, a strong anisotropy of the scattering pattern is observed, indicating the presence of long, thin and well-oriented cylinders in which the polymer is confined. Depending on the degree of polymerisation, either the polymer chain is elongated or several hairpins occur. The number of hairpins can be deduced from the comparison between the number of monomers in the polymer and the shape and size of the cylinder in which the main chain polymer is confined.

6. Neutron radiography

Neutron radiography is analogous to X-ray radiography [69,70] but offers the advantage of the larger penetration depth of neutrons in most elements, enabling us to probe through thick walls or containers of centimetre size or larger. This technique should be considered as an easy and efficient tool for non-destructive investigation of devices. It can be undertaken in reactor sources [69–71] as well as on spallation sources [72] and in some cases even using portable neutron sources. The large attenuation of the neutron beam by hydrogen or lithium can easily be used to visualize the materials containing these elements, such as the electrolyte inside batteries. This can be done to probe the electrolyte level [73] or to study the gas evolution on graphite electrodes [74] of lithium-ion batteries during charge/discharge cycling. Nowadays, the typical time scale accessible for neutron imaging technique is of the order of a second, but the use of stroboscopic[1] neutron imaging has also been developed enabling one to shorten the required exposure time down to typically 100 µs per image. This has allowed one to obtain the image of a four-stoke engine rotating at 1000 rpm and to follow the lubrification in situ by neutron radiography. Further details on this type of experiment can be found in Ref. [75]. Dynamic neutron radiography has also been used at the LLB reactor for the in situ and real time observation of spheres falling in a melt contained in crucibles [76,77]. Such experiments have been conducted at temperatures ranging from 1045 to 1100 °C.

7. In situ studies for archeometry

The usefulness of neutron scattering is now widely recognized in the field of archeometry, and several different experimental techniques have been used successfully to get information about archeological objects. Indeed, archeometry is a field where one needs non-destructive methods in order to probe museum objects or archeological findings. It is of particular interest in such a context to be able to investigate the interior of large objects without any damage. In general, the potential of neutrons to locate hidden materials and structures inside various objects has attracted the interest of archeologists and conservation scientists. Furthermore, the objects may be covered by coatings or corrosion layers and neutrons can thus be useful to probe the inner part of ancient objects. For example, neutron radiography [78] can be used to investigate the inner structure and details of the casting process of Roman bronze sculptures. Due to the high lead content and the consequently high absorption by X-rays, neutron imaging has been proved to be a unique technique to study throughout the volume of these types of objects by transmission. This technique is widely used in Switzerland where a systematic study of the roman bronze sculptures of the period 200 B.C.–300 A.D. is in progress [78,79]. In addition to neutron radiography, neutron diffraction can now be widely used to perform either phase identification or phase quantification. This has been undertaken for a large range of archeological objects. A non-destructive analysis of toilet accessories in Ancient Egypt has been carried out by neutron diffraction [2,80] at the Institut Laue–Langevin. The mixtures of chemical phases used at that time for the cosmetics have thus been determined and quantified in situ in their original container without any loss of powder and avoiding possible alteration due to reaction with air. Another example of such in situ neutron diffraction study is the characterisation of tin–lead medieval spoons from Amsterdam from the period 1350–1775 [81], for which the evolution of the Pb/Sn ratio has been related to different manufacturing processes and/or regulation of the lead content by the guild. This last example has been carried out on a pulsed source by time-of-flight neutron diffraction. For more information on the applications of this technique the reader should consult Ref. [81].

In addition to the phase quantification, powder diffraction pattern can also give information on the preferential orientation of the crystallites in polycrystalline samples. This technique, called texture analysis, may provide clues to the deformation history of the material, and hence to specific working processes. This can also be performed either by constant wavelength or by time-of-flight neutron diffraction and can consequently be performed both on reactors and on pulsed sources. A combined quantitative phase determination and texture analysis of Ag/Cu coins of the 16th century, revealed differences between minted and cast copies in terms of microstructures and silver/copper phases [81]. Whereas the genuine coins are minted and consequently show significant crystallographic textures, the forgeries are often cast copies. Thus, coins having irregular grain distributions were identified to be more likely faked ones. Another example of such technique is the investigation carried out at the ILL on the copper axe that was associated with the frozen mummy, nicknamed Ötzi, found in 1991 in the Schnalstal glacier (Similaun, Western Alps). This is the only known Copper-Age axe preserved with the original handle and bindings. Whereas the as-cast samples usually show a fibre texture, some of the prehistoric axes exhibit the so-called ‘cube texture’, which is nowadays known to be derived from cold-rolling of several metals, including copper and aluminium [82–84]. In general, the absence of the peculiar poles results from the recrystallisation of the twin boundaries of the copper crystallites, and indicates that the

---

[1] The stroboscopic acquisition mode is restricted to measurements of reversible phenomenon or processes that can repeated. In such cases, to achieve a reasonable signal-to-noise ratio and good reproducibility, the acquisition can be repeated over several periods until the counting statistics is sufficient to yield a reliable result. Such an acquisition mode enables one to shorten significantly the time scale accessible.

corresponding axes have not undergone significant recrystallisation. The in situ neutron diffraction texture analysis of the central portion of the Ötzi axe did not show any of the previous textures (neither fibre nor cube texture). This indicates extensive thermal annealing, probably due to several alternate cycles of cold working and thermal softening. This investigation has clearly revealed that skillful copper forging was already used at the time of the iceman Ötzi. The obtained texture maps go a long way in defining the metallurgical processes used to produce these important prehistoric tools and they are of great help in tracing the development of Alpine early metallurgy [84].

8. Time resolved studies

8.1. Time resolved studies by Small Angle Neutron Scattering

Thanks to the development of 'stopped-flow' techniques [85,86], the investigation in real time of fast kinetic processes can be achieved by small angle neutron scattering. The stopped-flow apparatus is designed to mix together small volumes of solutions in a very short time (10–90 ms) with good reproducibility. In order to increase the scattering intensity, new mixtures are injected repeatedly. The excellent reproducibility of the mixture allows one to perform stroboscopic SANS measurements, namely to add the scattering intensities provided by each mixture, at equivalent times.

An interesting example is the study of the formation of mesoporous silica from a supersaturated solution. Fig. 9 presents the time evolution of the SANS signal recorded for such measurements. The in situ SANS data were recorded on the instrument D22 at the ILL (Grenoble). This study has shown that formation of the silica based SBA-15 mesoporous system occurs in three-stages. First spherical micelles are formed, which, then, transform to elongated micelles, before packing together. The precipitation is witnessed by the appearance of the (10) peak at ca. 0.5 nm^{-1} in Fig. 9. This peak corresponds to the order between the silica cylinders and not to a local atomic order. The quantitative analysis of the SANS patterns can provide information on the shape and size of the micelles as well as on their respective time dependence in the early steps of the formation of this mesoporous material [85].

The same experimental technique has been successfully used to study the formation and growth of anionic vesicles [86,87]. In this case, a wide temporal scale, ranging from typically some one hundredths of a millisecond to a few hours was necessary. By following the radii of the vesicles it has been possible to show that their growth rate depends

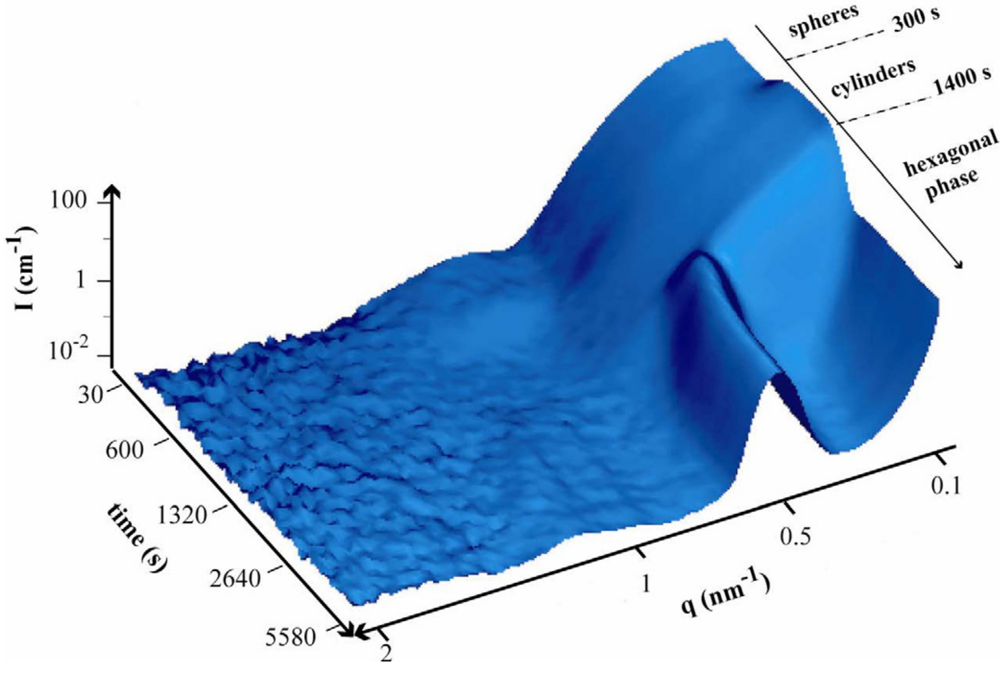


Fig. 9. The real time dependence of the Small Angle Neutron Scattering pattern recorded during the formation of the SBA-15 mesoporous material [85].

on the salt concentration, as well as on the ionic strength. A combined use of X-rays and neutrons has recently been reported by Né et al. to investigate the formation mechanism of the ZrO_2/surfactant mesophase nucleation [88]. The use of the stopped-flow technique [86,87] is thus very efficient and enables one to have a time resolution similar to that which can be achieved by SAXS on the best synchrotron radiation facilities. In such studies, the SANS neutron technique offers the advantage over X-rays to provide a large contrast between the micelles and the solvent.

8.2. Time resolved studies by powder neutron diffraction

An interesting example is the synthesis of the Ti_3SiC_2 compound which exhibits an unusual combination of metallic and ceramic properties. Indeed, this material has a peculiar structure that leads to thermal stability at high temperature, as in the case of ceramics, but also conducts heat and electricity like a metal. In addition, its good mechanical properties combined with a reasonable resistance to oxidation makes the Ti_3SiC_2 compound an excellent candidate material for high temperature applications such as jet engine turbine blades. Because of the difficulty of obtaining this ternary carbide as a pure phase, several synthesis processes have been tried over the years, many of which being investigated by in situ neutron diffraction. Since these synthesis processes have a wide range of kinetics, Kisi and Riley have investigated them over more than four decades of time resolution [89–92].

At heating rates of about 10 °C/min, the synthesis occurs via the conventional reactive sintering [91]. Such reactions have been investigated with a typical time scale of 2–20 min [91]. The investigated synthesis route was 3Ti/SiC/C reactive sintering to form the ternary Ti_3SiC_2 carbide. In this case neutron diffraction investigation has shown the occurrence of two intermediate phases: TiC_x and $Ti_5Si_3C_x$ [91], which are formed just after the hcp → bcc transformation of Ti. This process is rather slow and needs about 20 minutes at 1500 °C for completion of the Ti_3SiC_2 synthesis. The study of the time dependence of the different phases gives information on the kinetics of the reaction. Such a study has also been performed at the ISIS pulsed neutron source [89] using the time-of-flight technique (POLARIS instrument), enabling a diffraction pattern to be recorded in less than 3 minutes. Quantitative Rietveld analysis of the diffraction patterns allowed the identification of the intermediate phases, their quantification, the study of the kinetics of the ternary carbide formation and of the crystallization rate. Recently the instrument GEM [25,26,29] has been specially developed for in situ and time resolved materials science investigations. GEM uses a large detector array which covers a very wide range of scattering angles and a large solid angle of 4.0 steradians, enabling fast acquisition. The performance of GEM is comparable to that of D20 installed at the Institut Laue–Langevin, demonstrating that pulsed (spallation) sources and continuous (reactor) sources can now both provide useful instruments for time resolved studies.

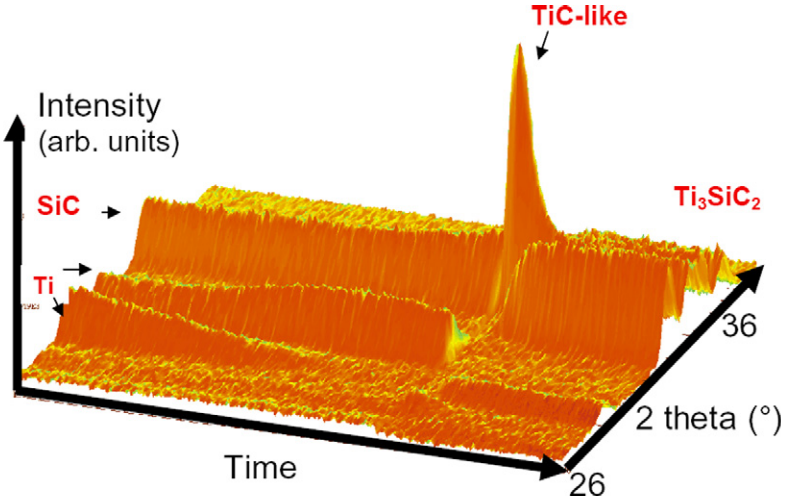


Fig. 10. Evolution of part of the diffraction pattern following the SHS reaction progression versus time with a 500 ms acquisition per diffraction pattern [90]. The total duration of the above evolution was about 110 seconds. During this part of the process, the temperature started from 900 °C to reach about 2500 °C.

The study of the fast synthesis process of Ti_3SiC_2 has been performed with a time resolution of a fraction of second on D20. This involved a self-propagating high-temperature synthesis (SHS) from Ti/SiC/C mixtures. A high acquisition data rate down to 300 ms per diffraction pattern has been used to follow the SHS from elemental starting materials, which involves a vigorous combustion reaction [90]. A typical example of the time evolution of the diffraction pattern is given in Fig. 10. This study has revealed five different stages in the SHS process,[2] whose detailed description can be found in Ref. [90]. These stages differ significantly from the one reported for the conventional reactive sintering. In the SHS case, the combustion reaction is initiated very rapidly, after the α (hcp) $\rightarrow$ β(bcc) Ti phase transformation, seen on the left part of the diffraction pattern given in Fig. 10. This happens at temperatures above 880 °C when the pre-ignition reactions occur, consisting of a local reaction of Ti with free C in the sample. Then, suddenly, an unexpected single solid intermediate phase appears within $\sim$0.5 s. This intermediate phase persists for 6 seconds, before nucleation and growth of the product Ti_3SiC_2 phase begin. The composition of the intermediate phase has been estimated to be a Si solution in a TiC-like structure. However, unlike what was reported for the low speed conventional reactive sintering, the coexistence of the two intermediate TiC_x and $Ti_5Si_3C_x$ phases has not been observed. During the SHS investigation, temperatures as high as 2500 K have been reached. This experiment has demonstrated the power of in situ neutron diffraction to reveal the reaction mechanism and the structural details of very fast synthesis processes. In such an investigation, a high data acquisition rate is essential to determine the different stages and phases present in the synthesis. In particular, the presence of a liquid phase has been ruled out during this SHS process. For long time, the self-propagating high-temperature synthesis has been difficult to investigate by in situ and time resolved methods except at high intensity synchrotron radiation facilities [93–95]. Such experiments are now possible at neutron sources as well, and one can benefit from the complementarities of neutrons and X-rays to better understand the mechanisms involved in the SHS process.

9. Conclusions

A wide range of neutron techniques is now available for scientists and engineers for in situ investigations in real conditions or even for time-resolved experiments. In situ studies can be performed, in principle, at many neutron sources, but due to limitation of neutron flux the time resolved experiments and in particular high-speed data acquisition are in practice often performed at high neutron flux reactors such as the Institut Laue–Langevin, or at the new pulsed sources, such as ISIS. During the last few years, a great development of instrumentation has led to the appearance of new spectrometers specially dedicated to these in situ or time resolved studies, like the powder diffractometer D20 at the ILL or GEM at ISIS, or the small-angle neutron scattering spectrometer D22. This has significantly broadened the range of time scales accessible, and it is now possible to investigate new phenomena with neutron scattering techniques. The construction of the next generation neutron pulsed sources will significantly improve the flux available at the sample position, thus enabling investigation of even faster processes than the ones presented above. This is one of the aims of the instrument to be constructed at the SNS (Oak-Ridge USA). It is worthwhile mentioning at this point that further improvements can also be achieved on the reactor facility: the Diffractometer for Rapid Acquisition over Ultra Large Angles (DRACULA) instrument project at the Institut Laue–Langevin will compete with the high flux SNS pulse source diffractometer [96,97]. Indeed, DRACULA will combine a larger neutron flux at the sample position (twice that of D20) with a larger solid angle of detection (1.5 steradian). Such instrument would consequently be an order of magnitude faster than D20 so that one can expect to obtain diffraction patterns in a matter of a few milliseconds. It will, of course, be particularly well dedicated for the study of kinetics of chemical reactions but could also be very useful to probe small samples of mm^3 size, under extreme conditions such as high pressure or temperature. We have seen that stroboscopic-type measurements can already be applied to several neutron techniques: small angle neutron scattering, powder diffraction, quasielastic or inelastic neutron scattering, thus giving already access to time resolutions of about a millisecond.

Other experimental techniques may present renewed interest for in situ studies, for example the triple axis neutron spectroscopy, in spite of the rather low neutron flux at the detector. It has been demonstrated that this technique can be adapted for investigation of kinetics during relaxation type experiments [2,3,98]. Although this method is limited

---

[2] Self-propagating high temperature synthesis is an extremely rapid, low cost and easy method to elaborate a large range of materials. However, because of the high kinetics of the synthesis, the composition and the physico-chemical characteristics of the final products are difficult to predict. Time-resolved diffraction studies are thus of prime importance to determine the mechanisms involved and control such synthesis processes.

to reversible processes as for most of the stroboscopic techniques, many different applications can be foreseen as described elsewhere [98]. Combining SANS and time resolved triple axis neutron spectroscopy, Eckold has studied the kinetics of spinodal decomposition in AgCl–NaCl single crystals [99,100]. The accessible time scales were found to range from 10^{-3} to 10^4 s. A time resolved study of the ferroelectric phase transition in Rb_2ZnC_{14} has been undertaken at a millisecond time scale by elastic neutron scattering [101,102]. Such a technique offers some advantages, such as good resolution and selectivity in reciprocal space. This could be used to study chemical solid solutions or modifications of lattice vibrations. More recently, time resolved inelastic neutron scattering has been successfully carried out to study the magnetization reversal in the Mn12ac single-molecule magnet using time of flight spectroscopy [103]. Such experiment enables to study the relaxation magnetization processes in magnetic compounds. In conclusion, the development of new experimental techniques for in situ or time resolved studies is naturally strongly connected with the progress of both neutron sources and instruments.

Acknowledgements

This article is dedicated to the memory of J. Pannetier, whose skills and enthusiasm have greatly contributed to the development of the in situ neutron diffraction studies in Europe.

The author would like to thank I. Grillo, A. Brûlet, H.E. Fischer and T. Hansen for interesting discussions and for providing some of the figures. My own collaborators are also warmly thanked for the in situ and/or the time resolved studies performed in common, in particular Y. Chabre and M. Latroche.

References

[1] J. Pannetier, Chemica Scripta 26 (1986) 131.
[2] O. Isnard, J. Optoelectron. Adv. Mater. 8 (2006) 411–417.
[3] O. Isnard, J. de Phys. IV 103 (2003) 133–171.
[4] M.C. Moron, J. Mater. Chem. 10 (2000) 2617–2626.
[5] O. Isnard, Usefulness of neutron scattering investigation in materials science, J. Optoelectron. Adv. Mater. (2007), in press.
[6] J. Pannetier, in: J. Baruchel, J.L. Hodeau, M. Lehmann, J.R. Regnard, C. Schlenker (Eds.), Neutron and Synchrotron Radiation for Condensed Matter, EDP-Sciences Publisher, 1993, p. 425.
[7] P.J. Withers, C.R. Physique (2007); DOI:10.1016/j.crhy.2007.09.015, in this issue.
[8] C. Fermon, F. Tasset (Eds.), Neutrons et magnétisme, J. de Phys. IV 89 (2001) 1.
[9] Yu.A. Izyumov, V.E. Naish, R.P. Ozerov, Neutron Diffraction and Magnetic Materials, Plenum Publishing Corp., 1991.
[10] O. Prokhnenko, et al., Neutron diffraction studies of the magnetic phase transitions in Ce_2Fe_{17} compound under pressure, J. Appl. Phys. 92 (1) (2002) 385–391.
[11] O. Prokhnenko, et al., Helimagnetic order in the re-entrant ferromagnet $Ce_2Fe_{15.3}Mn_{1.7}$, J. Appl. Phys. 97 (2005), 113909-1 to 8.
[12] J.L. Soubeyroux, N. Claret, Phys. A 74 (2002) S1025.
[13] J.L. Soubeyroux, J.M. Pelletier, R. Perrier de la Bâthie, Physica B 276–278 (2004) 905.
[14] P. Gorria, et al., Crystallisation and polymorphic transformations in Fe–Zr amorphous alloys obtained by high energy-ball milling, Physica B 350 (2004) e1075–e1077.
[15] X. Chuang-Dong, M. de Boissieu, J.M. Dubois, J. Pannetier, C. Janot, J. Mater. Sci. Lett. 8 (1989) 827–830.
[16] E. Chappel, M.D. Nunez-Regueiro, G. Chouteau, O. Isnard, C. Darie, Eur. Phys. J. B 17 (2000) 615–622.
[17] A.N. Christenesen, M.S. Lehmann, J. Pannetier, J. Appl. Cryst. 18 (1985) 170–172.
[18] M. Castellote, et al., Composition and microstructure changes of cement pastes upon heating as studied by neutron diffraction, Cement Concrete Res. 34 (2004) 1633–1644.
[19] A.N. Christensen, T.R. Jesen, J.C. Hanson, J. Sol. State Chem. 177 (2004) 1944–1951.
[20] J. Lyubina, et al., Ordering of nanocrystalline Fe–Pt alloys studied by in situ powder neutron diffraction, J. Appl. Phys. 100 (2006) 094308.
[21] J. Lyubina, et al., Influence of composition and order on the magnetism of Fe–Pt alloys: Neutron powder diffraction and theory, Appl. Phys. Lett. 89 (2006) 032506.
[22] O. Prokhnenko, et al., Effect of pressure and Mn substitution on the magnetic ordering of $Ce_2Fe_{17-x}Mn_x$, Appl. Phys. A 74 (2002) S610–S612.
[23] E.M.L. Chung, et al., Magnetic properties of tapiolite ($FeTa_2O_6$); a quasi two-dimensional (2D) antiferromagnet, J. Phys.: Condens. Matter 16 (2004) 7837–7852.
[24] E.J. Kinast, et al., Bicriticallity in $Fe_xCo_{1-x}Ta_2O_6$, Phys. Rev. Lett. 91 (2003), 197208-1.
[25] W.G. Williams, R.M. Ibberson, P. Day, J.E. Enderby, Physica B 241–243 (1998) 234–236.
[26] A.C. Hannon, Nuclear Instrum. Methods Phys. Res. A 551 (2005) 88–107.
[27] S.H. Kilcoyne, P. Manuel, C. Ritter, P. Radaelli, in: ILL Millenium Symposium Proceedings, 2001, pp. 170–171.
[28] S.H. Kilcoyne, Physica B: Condens. Matter 350 (2004) 91–97.

[29] P. Day, et al., GEM: The General Materials diffractometer at ISIS—multibank capabilities for studying crystalline and disordered materials, Neutron News 15 (2004) 19–23.

[30] H. Fischer, A.C. Barns, P.S. Salmon, Rep. Prog. Phys. 69 (2006) 233–299.

[31] O. Isnard, et al., Neutron diffraction study of the structural and magnetic properties of the $R_2Fe_{17}H_x$ ternary compounds (R = Ce, Nd, Ho), J. Less-Common Met. 162 (1990) 273–284.

[32] O. Isnard, et al., Neutron powder diffraction study of Pr_2Fe_{17} and $Pr_2Fe_{17}N_3$, Phys. Rev. B 45 (1992) 2920–2926.

[33] D. Fruchart, et al., R_2Fe_{17} and RM_{12} carbide and carbonitride synthesis from heavy hydrocarbon compounds, J. Alloys Comp. 203 (1994) 157–163.

[34] O. Isnard, et al., Neutron powder diffraction study of the desorption of deuterium in $Nd_2Fe_{17}D_{x=5}$, Physica B 180–181 (1992) 629–631.

[35] O. Isnard, et al., Magnetic circular X-ray dichroism study of the $Ce_2Fe_{17}H_x$ compounds, Phys. Rev. B 49 (1994) 15692–15701.

[36] E. Mamontov, et al., Neutron scattering study of hydrogen dynamics in $Pr_2Fe_{17}H_5$, Phys. Rev. B 70 (2004) 214305.

[37] T.J. Udovic, et al., Neutron vibrational spectroscopy of the Pr_2Fe_{17} based hydrides, J. Alloys Comp. 446–447 (2007) 504–507.

[38] O. Isnard, et al., Neutron powder diffraction study of the reaction of Nd_2Fe_{17} compound with nitrogen gas, Physica B 180–181 (1992) 624–626.

[39] Ph. Oleinek, et al., In situ neutron diffraction study of the reaction of the compounds $NdFe_{10.75}V_{1.25}$ and $NdFe_{11}Ti$ with nitrogen, J. Alloys Comp. 298 (2000) 220–225.

[40] B. Tolla, et al., Structural investigation of oxygen insertion within the $Ce_2Sn_2O_7$ and $Ce_2Sn_2O_8$ pyrochlore solid solution by means of in situ neutron diffraction experiments, J. Mater. Chem. 12 (1999) 3131–3136.

[41] J. Rodriguez-Carvajal, et al., The chemistry of $YBa_2Cu_3O_7$: a neutron powder thermodiffractometry study, Physica C 153–155 (1988) 1671–1672.

[42] M. Latroche, et al., In situ neutron diffraction study of deuterium absorption in AB_5 alloys used as negative electrode materials for Ni-MH battery, Physica B 350 (2004) E427–E430.

[43] L. Schlapbach, Hydrogen in intermetallic compounds I, Topics in Applied Physics serie 63, Springer-Verlag, Berlin, 1988, p. 350.

[44] L. Schlapbach, Hydrogen in intermetallic compounds II, Topics in Applied Physics serie 67, Springer-Verlag, Berlin, 1992, p. 328.

[45] M. Latroche, A. Percheron-Guegan, Y. Chabre, J. Alloys Comp. 293–295 (1999) 637.

[46] M. Latroche, et al., Influence of stoichiometry and composition on the structural and electrochemical properties of AB_{5+y}-based alloys used as negative electrode materials in Ni-MH batteries, J. Alloys Comp. 330–332 (2002) 787–791.

[47] S. Vivet, et al., Influence of composition on phase occurrence during charge process of AB_{5+x} Ni-MH negative electrode materials, Physica B 362 (2005) 199–207.

[48] F. Cuevas, et al., In situ neutron diffraction study of deuterium desorption from $LaNi_{5+x}$ ($x \sim 1$) alloy, Appl. Phys. A 74 (2002) S175–S177.

[49] F. Bardé, et al., *In situ* neutron powder diffraction of a nickel hydroxide electrode, Chem. Mater. 16 (2004) 3936–3948.

[50] Y. Chabre, Chemical physics of intercalation II, NATO Series B 305 (1993) 181–192.

[51] Y. Chabre, J. Pannetier, Progress Solid State Chem. 23 (1995) 1–130.

[52] M. Rippert, J. Pannetier, Y. Chabre, C. Poinsignon, Mat. Res. Soc. Proc. 210 (1991) 359–365.

[53] R.N. Vannier, et al., $Bi_4V_2O_{11}$ polymorph crystal structures related to their electrical properties, Solid State Ionics 157 (2003) 147–153.

[54] E. Capoen, et al., Time resolved in situ neutron diffraction investigation of the oxygen transfer in BIMEVOX membrane under operating conditions, Solid State Ionics 175 (2004) 419–424.

[55] V. Gerold, G. Kostorz, J. Appl. Cryst. 11 (1978) 376–404.

[56] J.P. Cotton, F. Nallet (Eds.), Diffusion des neutrons aux petits angles, J. de Phys. IV 60 (1999).

[57] R. Lund, et al., Equilibrium exchange kinetics in PEP-PEO block copolymer micelles. A time resolved SANS study, Physica B 385–386 (2006) 735–737.

[58] P. Damay, F. Leclercq, P. Chieux, A critical crossover in metal–ammonia solutions ($Na–ND_3$) as observed by small angle neutron scattering, J. Phys. Chem. 88 (1984) 3734–3740.

[59] J.N. Clark, M.L. Fernandez, P.E. Tomlins, J.S. Higgins, Macromolecules 26 (1993) 5897–5907.

[60] J.N. Clark, J.S. Higgins, C.K. Kim, D.R. Paul, Polymer 33 (1992) 3137–3144.

[61] D. Bellet, A. Royer, P. Bastie, J. Lajzerovicz, J.F. Legrand, In situ small angle neutron scattering study of γ' precipitates in AM1 supermalloy single crystals, in: S.D. Antolovich, et al. (Eds.), Supermalloy, The Minerals, Metals & Materials Society, 1992, pp. 547–553.

[62] M. Véron, P. Bastie, Acta Mater. 45 (1997) 3277.

[63] A. Royer, P. Bastie, D. Bellet, B. Hennion, Rev. Metal. Paris 93 (1996) 2.

[64] U. Cihak, et al., Characterization of residual stresses in turbine discs by neutron and high-energy X-ray diffraction and comparison to finite element modelling, Mater. Sci. Eng. A 437 (2006) 75–82.

[65] C. Pujolle-Robic, L. Noirez, Nature 409 (2001) 167–170.

[66] L. Noirez, Phys. Rev. Lett. 84 (2000) 2164–2167.

[67] M.H. Li, et al., Observation of hairpin defects in a nematic main chain polyester, Phys. Rev. Lett. 70 (1993) 2297–2300.

[68] M.H. Li, et al., Study of the chain conformation of thermotropic nematic main chain polyesters, J. Phys. II France (1994) 1843–1863.

[69] J.C. Domanus (Ed.), Practical Neutron Radiography, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992.

[70] G. Bayon, J. de Phys. IV 130 (2005) 231–241.

[71] M. Dierick, et al., High-speed neutron tomography of dynamic processes, Nucl. Instrum. Methods Phys. Res., Sect. A 542 (2005) 296–301.

[72] B. Schillinger, E.H. Lehmann, Neutrons News 17 (2006) 19–21.

[73] M. Lanz, et al., In situ neutron radiography of lithium-ion batteries during charge/discharge cycling, J. Power Sources 101 (2001) 177–181.

[74] D. Goers, et al., In situ neutron radiography of lithium-ion batteries: the gas evolution on graphite electrodes during the charging, J. Power Sources 130 (2004) 221–226.

[75] B. Schillinger, J. Brunner, E. Calzada, Physica B 385–386 (2006) 921–923.

[76] A. Khale, B. Winkler, B. Hennion, J. Non-Newtonian Fluid Mech. 112 (2003) 203–215.

[77] B. Winkler, et al., Neutron imaging and neutron tomography as non destructive tools to study bulk rock samples, Europ. J. Mineralogy 14 (2002) 349–354.

[78] E.H. Lehmann, Neutrons News 17 (2006) 22–29.

[79] E. Deschler-Erb, E.H. Lemann, M. Soares, Alt heydnisch Bildein von Ertz, Archeologie der Schweitz 27 (2004) 3.

[80] P. Martinetto, et al., in: G. Tsoucaris, J. Lipkowski (Eds.), Molecular and Structural Archeology: Cosmetic and Therapeutic Chemical, in: NATO Series, vol. 117, Kluwer Academic Press Publisher, 2003, p. 107.

[81] W. Kockelmann, Applications of TOF neutron diffraction in archaeometry, Appl. Phys. A: Mater. Sci. Process. 83 (2006) 175–182.

[82] G. Artioli, et al., Early copper alpine metallurgy, in: Proceedings of the International Conference on Archeometallurgy in Europe, 2003.

[83] G. Artioli, et al., Institut Laue–Langevin experimental report, www.ill.fr.

[84] G. Artioli, et al., Crystallographic texture analysis of the iceman and coeval copper axes by non invasive neutron powder diffraction, in: A. Fleckinger (Ed.), Die Gletschermumie aus der Kupferzeit 2, in: Schriften des Südtiroler Archeologiemuseums and Südtiroler Archeologiemuseum, Folio Verlag, Bozen/Wien, ISBN 3-85256-249-X/88-86857-41-1, 2003.

[85] M. Impéror-Clerc, et al., Initial steps of the formation of SBA-15 materials: an in situ small angle neutron scattering investigation, Chem. Comm. (2007) 834–836.

[86] I. Grillo, J. Phys. IV France 130 (2005) 75.

[87] I. Grillo, E.I. Kats, A.R. Muratov, Langmuir 19 (2003) 4513–4581.

[88] F. Né, et al., How does ZrO_2/surfactant mesophase nucleate? Formation mechanism, Langmuir 19 (2003) 8503–8510.

[89] E. Wu, D.P. Riley, E.H. Kisi, R.I. Smith, Reaction kinetics in Ti_3SiC_2 synthesis studied by time resolved neutron diffraction, J. Europ. Ceram. Soc. 25 (2005) 3503–3508.

[90] D.P. Riley, E.H. Kisi, T.C. Hansen, A.W. Hewat, Self-propagating high temperature synthesis of Ti_3SiC_2: Ultra high speed neutron diffraction study of the reaction mechanism, J. Am. Ceram. Soc. 85 (2002) 2417–2424.

[91] E. Wu, E.H. Kisi, S.J. Kennedy, A.J. Studer, In situ neutron diffraction study of Ti_3SiC_2 synthesis, J. Am. Ceram. Soc. 84 (2001) 2281–2288.

[92] E. Wu, E.H. Kisi, S.J. Kennedy, R.I. Smith, Intermediate phases in Ti_3SiC_2 synthesis from Ti/SiC mixtures studied by time-resolved neutron diffraction, J. Am. Ceram. Soc. 85 (2002) 3084–3086.

[93] J. Wong, et al., Time resolved diffraction study of solid combustions reactions using synchrotron reaction, Science 249 (1990) 1406.

[94] C. Curfs, TiC–NiAl composites obtained by SHS: a time resolved XRD study, J. Europ. Ceram. Soc. 22 (2006) 1039–1044.

[95] L. Contreras, et al., Time resolved XRD study if TiC–TiB_2 composites obtained by SHS, Acta Mater. 37 (2004) 4783–4790.

[96] A.W. Hewat, H.E. Fischer, B. Guerard, M. Thomas, Dracula and the H12 tube renewal, project in preparation.

[97] H.E. Fischer, A.W. Hewat, DRACULA internal report, Institut Laue–Langevin, September 2006.

[98] G. Eckold, Nucl. Instrum. Meth. A 238 (1990) 221–230.

[99] G. Eckold, J. Phys. Condens. Matter 13 (2001) 217–220.

[100] A. Ringe, P. Elter, H. Gibhardt, G. Eckold, Sol. State Ionics 177 (2006) 2473–2479.

[101] U. Steigenberger, G. Eckold, M. Hagen, Physica B 213–214 (1995) 1012–1016.

[102] U. Steigenberger, G. Eckold, M. Hagen, Nucl. Instrum. Meth. B 93 (1994) 316–321.

[103] O. Waldmann, et al., Magnetic relaxation studies on single-molecule magnet by time-resolved inelastic scattering, Appl. Phys. Lett. 88 (2006) 042507.