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Invited Lecture

In situ and/or time resolved powder neutron scattering for materials science

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In general, neutrons offer the advantage to be weakly absorbed by materials. Consequently neutron scattering is a very efficient tool to probe deeply inside the materials in a non destructive manner. Time resolved neutron scattering is thus widely used by different scientific communities: materials science, physics, chemistry… It is now possible to perform neutron diffraction in situ, in complex environments: electrochemical reaction cells, pressure cells… In situ neutron diffraction has been widely developed on high neutron flux sources such as the Institut Laue Langevin (Grenoble). Neutron scattering is a very useful technique for time resolved reaction processes inside materials. The experimental set-up needed for such type of experiments is briefly presented. Thereafter, examples of recent applications of neutron diffraction are described to illustrate the possible use of thermodiffractometry, in situ and/or time resolved to investigate phase transitions of chemical processes. The examples are taken in different scientific fields: metallurgy, electrochemistry, magnetism, solid state chemistry, archeometry.

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1. Introduction

Powder diffraction is a well known and useful non destructive technique for identifying and characterizing crystalline solid materials. X-ray powder diffraction is by far the most often used method since it is simplest and less expensive but neutron beam can also be used and can offer many advantages. For a detailed comparison of the two different radiations of the reader can refer to general books and review such as [1,2]. Without going into details it is worthwhile to mention some of the specificities of neutrons scattering.

An advantage of neutrons is the low absorption cross section of most elements; this is useful when the sample has to be contained in a controlled environment such as furnaces, cryostat, high pressure cell or reaction cell. Indeed the neutron beam can go through rather thick sample container without being completely absorbed and be scattered by the sample. If generally X-rays can only see thin layers at the surface of the sample, neutrons can probe much deeper and give information about bulk sample in a non destructive manner. In terms of crystallography, the main advantage of neutrons against X-rays is that they are generally more sensitive to the position of light atoms because the neutron scattering amplitude does not show a strong dependence on the atomic weight. This leads to more accuracy in locating lights elements (hydrogen, carbon, oxygen, fluorine…) even in the vicinity of heavy atoms like lead, uranium … It is well known that the X-ray scattering amplitude of atoms that are adjacent (Fe and Co for example) in the periodic table are almost the same so that these atoms are very difficult to distinguish. In most cases this is much easier with neutrons, since there is more contrast in their scattering amplitudes. Finally the high sensitivity of neutrons scattering to the magnetism is another advantage in order to investigate magnetic materials. For more details on the neutrons scattering and its use in materials science, the reader can refer to [1,3].

The purpose of this article is to illustrate the potential of neutron powder diffraction in different field of material science with an emphasis on in situ and time resolved experiments. After a brief presentation of the experimental set-up, we will give examples of neutron powder diffraction investigation. The examples are taken in different field of material science, physics, chemistry, magnetism… The use of thermodiffractometry to follow phase transitions will be described. Then examples of in situ studies of chemical reaction will be presented as well as the use of time resolved neutron diffraction to investigate kinetic phenomena. Finally the possibility to perform in situ or time resolved studies using other neutron techniques will be briefly commented.

2. Experimental

In order to perform in situ studies by powder diffraction the ideal case is to be able to record a good diffraction pattern (with adequate statistical accuracy) in a short time. Then the investigation can be extended to study time dependant phenomenon if the acquisition time is much shorter than the characteristic time of the process. From the experimental point of view the requirements are as follow:

1) A high neutron flux at the sample position is needed.

2) A large detector has to cover a wide diffraction range in order to collect a complete diffraction pattern as fast as possible. A high efficiency of the neutron detection is also needed.

An example of such instrument is shown in Fig. 1, this D1B instrument is operating at the high flux reactor of the Institut Laue Langevin (Grenoble) [4]. D1B is a two-axis spectrometer installed on a thermal neutron guide operating with wavelength of either 1.28 or 2.52 Å. This instrument is composed of a large position sensitive detector (PSD) covering an angular range of 80° (2theta) which can be moved in an angular range of $2° < 2\theta < 140$. The PSD is a multidetector composed of 400 ^{3}He/Xe detectors.

Due to the combination of a high flux neutron source and a PSD, powder diffraction pattern can be recorded at a time scale of about one to a few minutes. D1B is consequently an excellent instrument to perform in situ analysis and time resolved diffraction experiments since this time scale is adapted to the kinetics of many physical or chemical processes. This type of instrument is also very powerful to study magnetic structures in condensed matter. The Institut Laue Langevin has also constructed another instrument called D20 where diffraction pattern can even be recorded at a time scale of a few seconds [3,4].

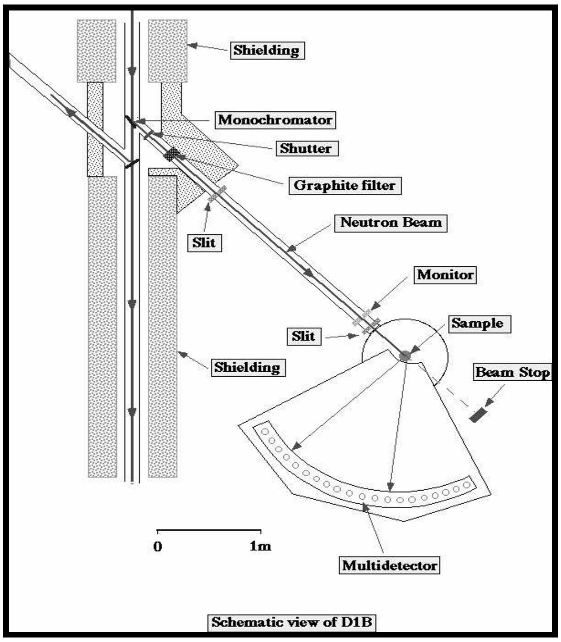


Fig. 1. Schematic description of D1B a powder neutron spectrometer at the Institute Laue Langevin.

3. Thermodiffractometry

Bulk metallic glasses are intermetallic alloys exhibiting an amorphous structure and that can be produce in dimension much larger than millimetres. For a long time these materials were produce by high cooling rate 10^6 K.s^{-1}. In the last decade, alloy compositions have been discovered enabling to obtain bulk metallic glasses with much lower cooling rate of a few 0.1 Ks^{-1}. The new families [5,6] of bulk metallic glasses offers excellent opportunities for studying the glass transition in particular the glass transition that can be probed over a wide speed range. Last but not least, some of these new alloys are exhibiting interesting mechanical properties in the glass state and are industrially used.

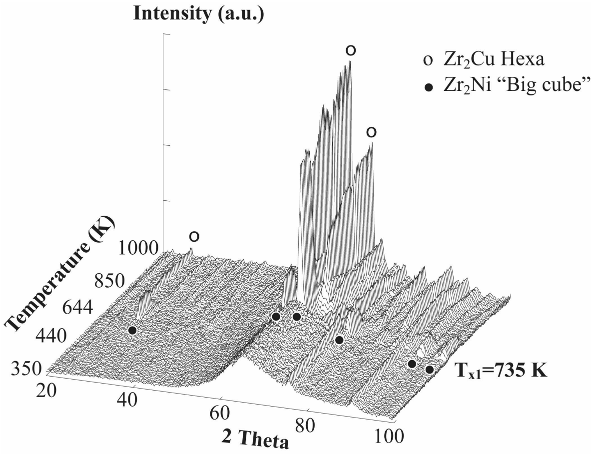


Fig. 2. Thermal evolution of the neutron powder diffraction pattern upon heating (at a rate of 2 K/minutes) an amorphous alloy of Zr-Ti-Cu-Al-Ni type [7].

In order to illustrate the use of in situ neutron diffraction experiment to investigate the crystallization behavior of bulk metallic glasses by in-situ neutron diffraction, Fig. 2 represents the thermal evolution of the powder neutron diffraction pattern of a Zr-Ti-Cu-Al-Ni type alloy. The appearance of diffraction lines on the pattern is in good correspondence with the exothermic peaks on the DSC – Fig. 3. The origin of the different anomaly observed on the DSC analysis can be better understood by comparison with the thermodiffraction pattern recorded in situ and measured at the same heating speed of 2 K/minute [7]. Combination of both techniques leads to a much better understanding of the phenomenon involved during the heating.

The first modification of the diffraction pattern appears at T_{x1}, temperature that corresponds to the onset of crystallization. The first phase to crystallize has sharp diffraction lines corresponding to large crystals of Zr_2Ni. This phase is found to be transitory and disappears when the main crystallization appears (at c.a. 873 K) thus leading to phase separation. Among the different phases involved in the crystallization process ($(Zr(NiCu))_{10}$ and Zr_2Cu), the diffraction peaks of the Zr_2Cu hexagonal phase are shown in Fig. 2. Other examples of such type of study can be found in reference [7] and [8]. Such analysis not only helps to better control (avoid) the crystallization of the phases but also contributes to the understanding of the thermodynamic properties of the bulk magnetic glasses.

This knowledge can be used to improve of the synthesis of these high mechanical properties bulb metallic glasses.

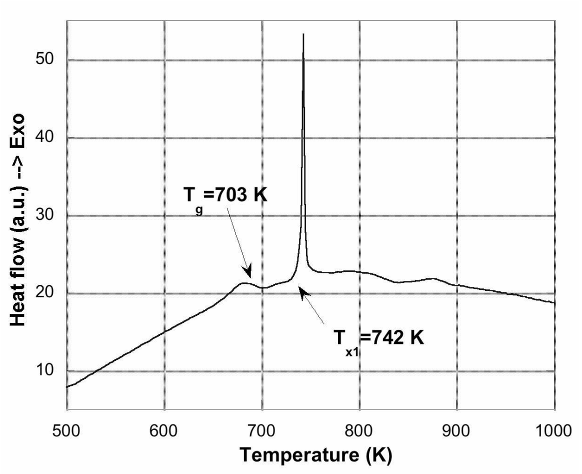


Fig. 3. DSC analysis performed under the same condition for the Zr-Ti-Cu-Al-Ni type alloy [7].

This type of real time neutron diffraction study can be extended to many other classes of materials. It has also been performed successfully to investigate the formation of icosahedral alloys, leading to a better understanding of the mechanism involved in the formation of AlCuFe, AlPdMn quasicrystals [9,10].

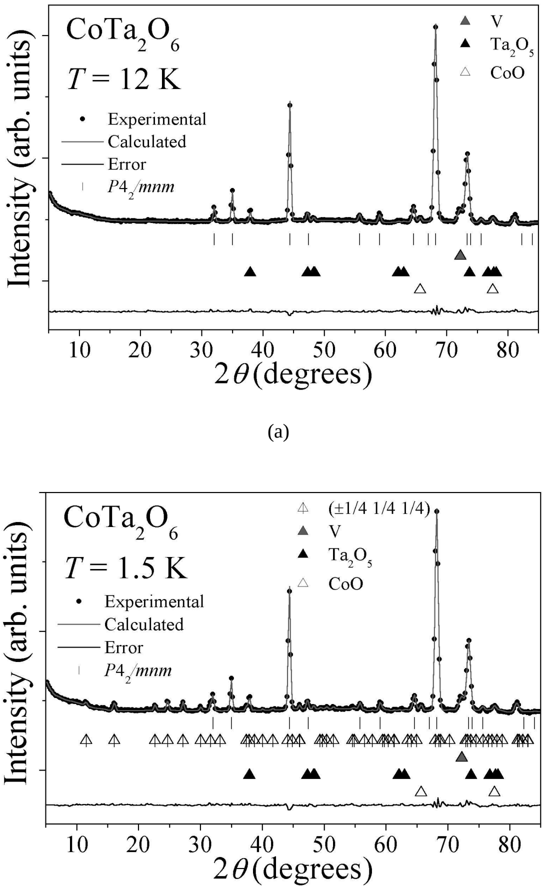
4. Magnetic phase transition studies by powder neutron diffraction

Neutron diffraction is the ideal tool to determine the magnetic structure in compounds. Since the pioneer discovery of the antiferromagnetic order in MnO many different structures have been determined. For more details on the magnetic structures and their determination by neutron diffraction one can refer to the following references [11-13]. In order to briefly illustrate the usefulness of this technique, we will give two examples.

Fig. 4 presents a comparison of the neutron powder diffraction pattern recorded at 12 and 1.6 K for $CoTa_2O_6$. The temperatures have been chosen above and below the ordering temperature of $CoTa_2O_6$ respectively [14,15]. At 1.6 K, it is observed that additional Bragg reflections are appearing. Consequently, these Bragg peaks are purely of magnetic origin. The indexation of these Bragg reflections leads to a large magnetic cell 4×4×4 times larger than the crystalline unit cell. A drawing of this magnetic structure is plotted in Fig. 5-a. [14,15].

In a second example given in Fig. 5-b, the observation of the thermal evolution of the MnRhAs diffraction pattern shows that in addition to the three diffraction peak (100), (001) and (110) due to the crystal structure many Bragg peaks due to the magnetic structure are appearing at low temperature. The presence of the (001/4) reflection below 141 K bears witness to a magnetic cell four time larger along the c axis that the crystal structure. This magnetic order is characterized by a propagation vector ($00q_z$) with $q_z=1/4$. At higher temperature a magnetic phase transition occurs, this (001/4) peak disappears whereas a new peak of (001/2) appears at about 162 K, This transition between two different magnetic state occurs progressively since a gradual decrease of the (001/4) intensity is observed. It is worth to notice that during the transition an intermediate state is observed with satellite peaks appearing then disappearing at (001/4-z) and (001/4+z).

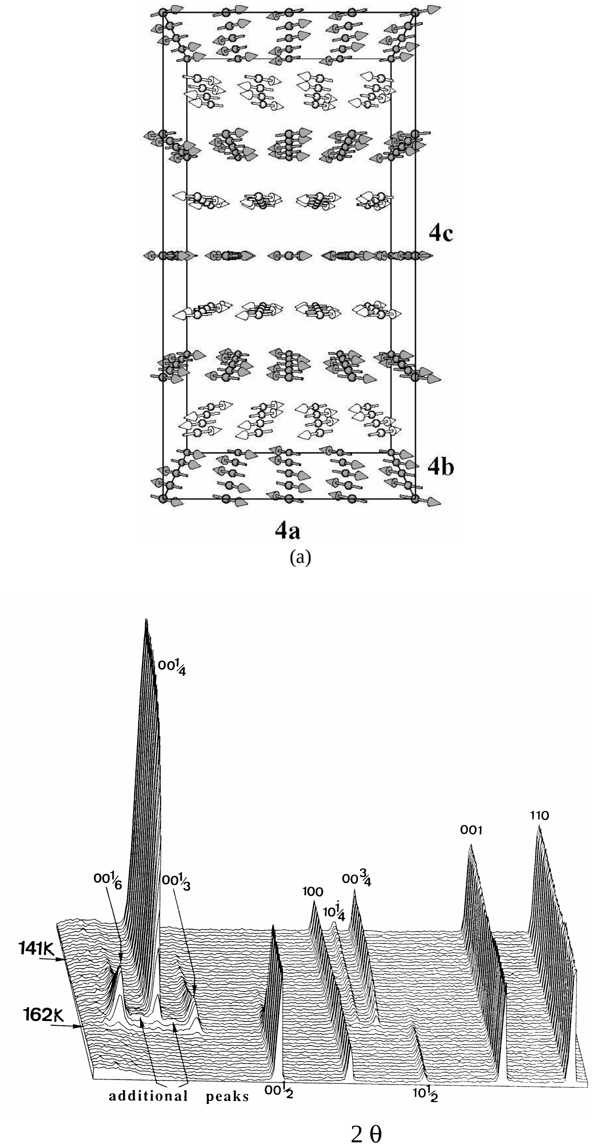
The details of the complex magnetic structures observed for MnRhAs can be found in reference [16]. Whithout going into such detailed description, this example illustrates that a simple thermodiffraction experiment can give many fruitful information on the magnetic phase diagram of materials.



(a)

(b)

Fig. 4. Comparison of the neutron powder diffraction pattern recorded at 12 (a) and 1.6 K (b) corresponding to above and below the ordering temperature of $CoTa_2O_6$ respectively [14,15].



(a)

(b)

Fig. 5. Magnetic structure retained by $CoTa_2O_6$ at 1.5 K (a) [14,15]. Thermal behaviour of the neutron scattering spectra obtained from a powder of MnRhAs in the vicinity of the magnetic phase transition [16].

5. In situ study of chemical process: solid-gas reaction

In situ investigation of solid gas reaction, has been performed in order to analyse the insertion of light element (H, C, N) within the crystal lattice of the R_2Fe_{17} type phases (R being a rare earth element) [17,18,19,20]. The evolution of the neutron powder diffraction pattern during the reaction of Ho_2Fe_{17} with anthracene is plotted in Fig. 6 [20]. It is worth to note that the oscillations of the background are due to the reaction cell used made of amorphous silica. A whole diffraction pattern has been recorded every five minutes. As can be seen from Fig. 6 during the reaction of Ho_2Fe_{17} with anthracene at 713 K, the diffraction pattern evolves from that of pure Ho_2Fe_{17} towards a mixture of Ho_2Fe_{17} and $Ho_2Fe_{17}C_x$ phases. For clarity, some of the diffraction peaks corresponding to the phase $Ho_2Fe_{17}C_x$ are labelled by a cross in Fig. 6. The hexagonal crystal symmetry of the Ho_2Fe_{17} phase is kept upon carbon insertion. The time evolution of the intensity of these peaks can easily enable to determine the kinetic of the reaction. After 300 minutes at 713 K forty percent of the starting Ho_2Fe_{17} compound was already transformed into the corresponding carbide $Ho_2Fe_{17}C_x$. The location of the diffraction peaks are characteristics of the unit cell volume and can be followed during the reaction.

The Rietveld analysis of each diffraction pattern has permitted to determine precisely the location of the interstitial atoms and to better understand the chemical reaction. The carbon atoms are filling octahedral interstitial sites in the holmium neighbourhood leading to a stœchiometry of $Ho_2Fe_{17}C_{2.8}$ [20]. No hydrogen is found to be accommodated in the structure under these experimental conditions. The chemical process observed at 713 K can be described by the following reaction:

$$5\ Ho_2Fe_{17} + C_{14}H_{10} \Rightarrow 5\ Ho_2Fe_{17}C_{2.8} + 5\ H_2 \qquad (1)$$

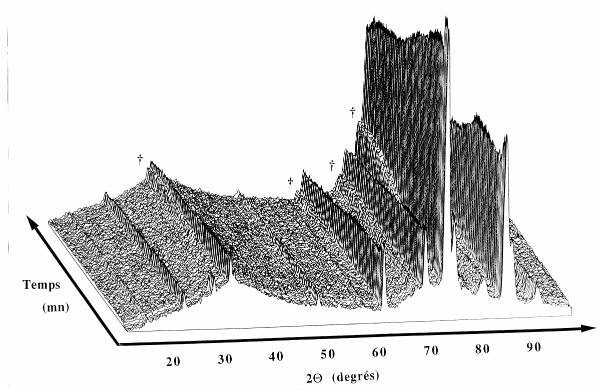
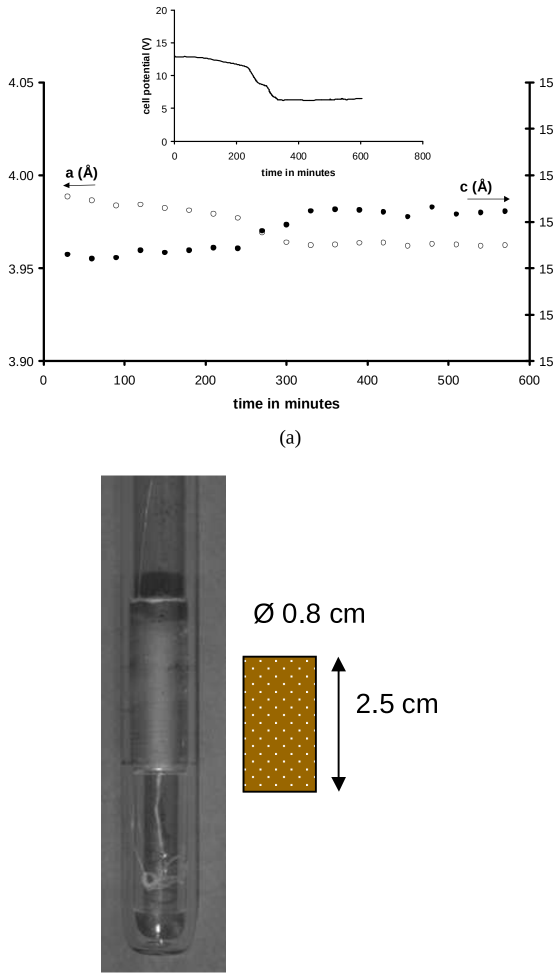


Fig. 6. Neutron thermodiffraction patterns recorded during the reaction of Ho_2Fe_{17} with anthracene [20].

This type of studies has been also used for many other chemical processes such as the investigation of oxygen exchange properties of different materials. This has been successfully used to investigate the oxygen storage capacity in the $Ce_2Sn_2O_7$ compound. This pyrochlore phase was found to accommodate up to one additional oxygen atom, whose insertion process and atomic location has been determined by in situ neutron diffraction study [21]. A solid solution $Ce_2Sn_2O_7$ - $Ce_2Sn_2O_8$ was analysed showing a high oxygen exchange at low temperature. Oxygen insertion was found to occur in two different atomic sites, thus leading to two successive de-insertion reactions [21].

6. Time resolved investigation of electrochemical reactions

High oxygen fluxes can be obtained with electrically driven $Bi_4V_2O_{11}$ type ceramic (BIMEVOX) membranes simply made of a dense electrolyte sandwich in between two gold grids as current collectors. Cylindrical membranes (8 mm in diameter, 2.5 cm in thickness, see Fig. 7) made with a composite containing 20% (or 40%) in volume of gold and 80% (60%) of $Bi_4V_2O_{11}$ (the parent compound of BIMEVOX materials) or BICOVOX.10 ($Bi_2V_{0.9}Co_{0.1}O_{5.35}$) ceramic were prepared. Gold wires were stuck on both faces. They were characterized under polarization by in situ neutron powder diffraction on the D1B diffractometer at a wavelength of 1.28 Å. To perform the experiment under air atmosphere, the cell was introduced in a quartz tube open to air which was placed in a furnace. The studies were performed at 620 °C. The time resolved in situ investigation has been undertaken under operating conditions and the electrochemical parameters were controlled during the process [22]. The unit cell evolution of the 20% gold cermet $Bi_4V_2O_{11}$ membrane under a 200 mA is plotted versus time in Fig. 7. The time dependence of the potential of the electrochemistry cell is plotted as inset in the same figure. This clearly shows that structural changes are occurring during the process.



(a)

(b)

Fig. 7. Time dependence of the unit-cell parameters for a 20% gold cermet $Bi_4V_2O_{11}$ membrane under a 200 mA applied current (a) a photo of the membrane in the silica cell is given in (b) together with a schematic drawing [22].

Under current, the diffraction pattern given in Fig. 8 reveals that the bi-dimensional structure of BIMEVOX is maintained during the process. The Rietveld analysis shows that the changes observed in the diffraction pattern are connected to a small reduction of the electrolyte from V^{5+} into V^{4+} is observed. This allows the oxygen transfer at the surface of the membrane under working conditions. Neutron diffraction revealed that this is not limited to the cathodic surface of the membrane but occurs in the entire membrane. The transformation is found to be reversible. More details on the operating conditions and the analysis can be found in references [22].

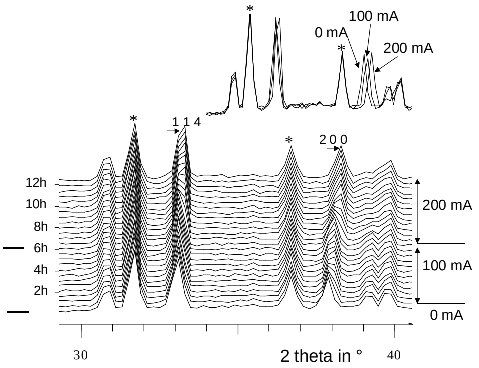


Fig. 8. Neutron diffractograms collected every 30 minutes at the interface on a 40 volume percent gold-$Bi_4V_2O_{11}$ cermet and pure $Bi_4V_2O_{11}$ membrane (BI40G-BI) before polarization, under 100 mA and 200 mA electrical bias (stars indicate gold Bragg peaks). Wavelength of 1.28 Å [22].

In situ neutron diffraction has also been used to investigate the electrochemical behaviour of Ni-MH batteries. Many researches has been devoted to study hydrogen absorption in AB_{5+y} alloys used as negative electrode materials [23-26]. More recently the behaviour of the positive nickel hydroxide electrode [27,28] has also been probed in situ. For these studies a special electrochemical cell devoted to in situ neutron diffraction experiments has been developed whose description can be found eslsewhere [23,27].

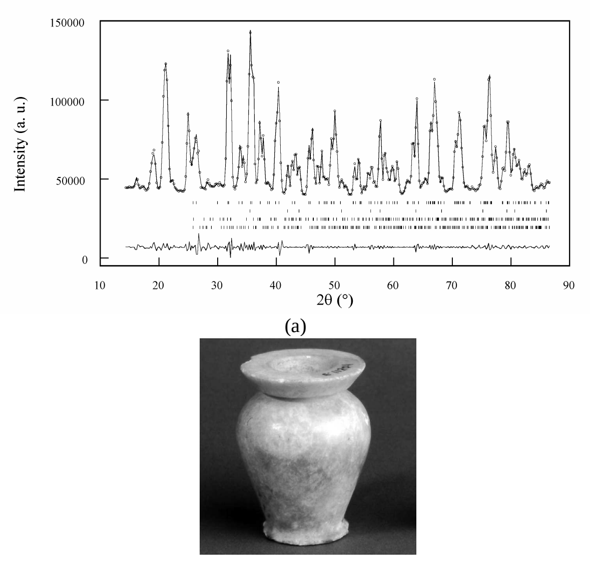
For more details on the experimental procedure and /or other examples of possible time resolved in situ neutron diffraction during chemical reactions see the following references [1,29-31].

7. In situ study in archeometry

Neutron diffraction experiments can also be used in situ in archaeology. Indeed, because of the large penetration of neutrons, sample can be probed even in big container. Furthermore the fact that this method is non destructive is also very important in archeometry where sampling is often impracticable or unacceptable. A non-destructive analysis of toilet accessories in Ancient Egypt has been carried out by neutron diffraction [32]. The mains advantages of the techniques are: to avoid the extraction of cosmetic powder from their archaeological container and to avoid the waste of powder. Furthermore due to either chemical alteration or local contamination, the composition of the samples extracted may be different from the top surface or at the centre or over the inner walls of the container. To address this problem, the powder inside the toilet accessories was directly analyzed by neutron diffraction. The aims of such an experiment were: i) adapting and optimizing a non destructive technique for the quantitative analysis with no sampling and no external contamination ii) testing the homogeneity of the cosmetic mixture at different locations inside the container without sampling the powder at different regions.

Six recipients of two different nature (reeds and stoned vases) have been investigated, the powder sample has been analysed at different location points [32]. The neutron beam was directed towards the regions of interest. In spite of the large scattering coming from the container see Fig. 9, it has been possible to determine the nature and the percentages of the different crystalline phases involved in the cosmetic: PbS,$PbCo_3$ and $Pb_2Cl_2CO_3$ [32].

As can be seen from the diffraction pattern plotted Fig. 9, another difficulty is that the Bragg lines of the calcite container are partly overlapping the ones of the cosmetic sample. It was also possible to check that the mineral composition of the powder does not present any noticeable variation and does not depend on the position of the analyzed region inside the pot. These results rule out any transformation of the as-found mineral ingredients. The effects on the powder composition of ageing, alteration, watering (action of salts for example) could not be detected. This study gives an example of the capability of neutron techniques to study non-destructively objects of our cultural heritage. Many other applications of neutron diffraction in archeometry can be use as can be seen from the following references [33]. One of the most common use it the texture analysis which may provide clues to the deformation history of the material, and hence to specific working processes.



(a)

(b)

Fig. 9. In situ neutron diffraction pattern of the Ancient Egypt cosmetic sample (a) contained in the calcite vase shown on the right (b) [32].

8. Conclusions

As has been discussed above, powder neutron diffraction is a powerful tool that can be use for many research fields of the material science community. This technique has been widely developed on high neutron flux sources. In situ but also time resolved experiments can now be performed in many different scientific field: metallurgy, electrochemistry, magnetism, solid state chemistry, archeometry…

Recent instrumental developments have led to a significant improvement of other neutron techniques and a dramatic decrease of the acquisition time even for single crystal diffraction using a polychromatic beam. Indeed time resolved experiment can now be performed at a scale of a few minutes using the Laue type instrument VIVALDI newly developed at the Institut Laue Langevin [4,34]. Such method has now proved its efficiency to investigate phase transformation [35] in single crystal sample. Small Angle Neutron Scattering (SANS) is also now able to follow in situ processes in materials sciences. For example, in situ experiments have been performed using SANS to study the coalescence and the precipitation of the γ' phase in nickel based superalloy single crystals. The influence of the cooling rate on the precipitation has been analyzed as well at the kinetics of the growth of the precipitates [36].

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