Time-of-Flight Neutron Diffraction (TOF-ND) for Characterising Archaeological Artefacts

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1. Introduction

Neutrons are, as building blocks of all atoms except ordinary hydrogen, basically everywhere. Free neutrons, however, are only produced in nuclear reactions and used as versatile microscopic probes to study material properties of solids at an atomic level. Neutrons are usually not the first choice for archaeometric analyses probably because they are almost exclusively produced and applied at large-scale facilities. It certainly requires some effort and convincing reasons to take an archaeological object to a neutron centre for analysis. Traditionally neutrons are produced in nuclear research reactors, for example at the Institute-Laue-Langevin in Grenoble, France. Nowadays neutrons are also generated with neutron spallation sources that are based on high-energy particle accelerators, like the ISIS facility at the Rutherford Appleton Laboratory, UK. The future of neutron production will probably go along the lines of the spallation technology, and the constructions of new powerful spallation sources have already started in the United States and Japan.

Neutrons are of particular interest for material scientists because they allow for non-destructive testing of a big and intact object, be it an engineering component such as a turbine blade or a museum object such as a prehistoric copper axe (Rinaldi, 2002). The relevant property for the material testing is penetration power: neutrons pass through centimetre thick metal objects without problem and deliver high contrast information from the interior. The unique interaction properties of the neutron probe with matter are exploited for several applications in forensic and archaeometric sciences. Neutron Activation Analysis (NAA) makes use of the radio-activation potential of neutrons for determining tiny amounts of chemical elements in archaeological materials. NAA is usually used for provenance studies of ceramics which are exposed to a high intensity neutron beam. The activated material emits gamma rays at energies that are specific for the chemical elements present in the material. Neutron radiography (NR) is able to display inner features of artefacts by utilising the generally high penetration potential and combining it with the selective neutron absorption by different chemical elements. High contrast

imaging is further enhanced if three-dimensional tomography images are reconstructed from a sequence of radiographs recorded for different object orientations. Neutron diffraction (ND) is based on the reflections of neutrons by a crystalline material and is a direct method for examining all structural aspects of a material. The diffraction pattern contains information on the microscopic structure of an artefact, i.e. the arrangement of atoms and the arrangement of grains, which in turn is related to its making technique. Neutron diffraction has much in common with and, at the same time, is in many ways complementary to the other fundamental method for structure research: X-ray diffraction. Actually, neutrons and X-rays permit to see a material in a different "light" due to the very different interaction mechanisms in matter.

2. Neutron properties and neutron production

The neutron as a nuclear constituent is stable. The free neutron, however, is a radioactive particle that decays into proton, electron, and anti-neutrino after an average lifetime of 15 minutes. The life of neutrons is long enough for them to be used as diagnostic probes in fundamental and material sciences. At first however, neutrons have to be released from the nuclei either by nuclear fission or by spallation.

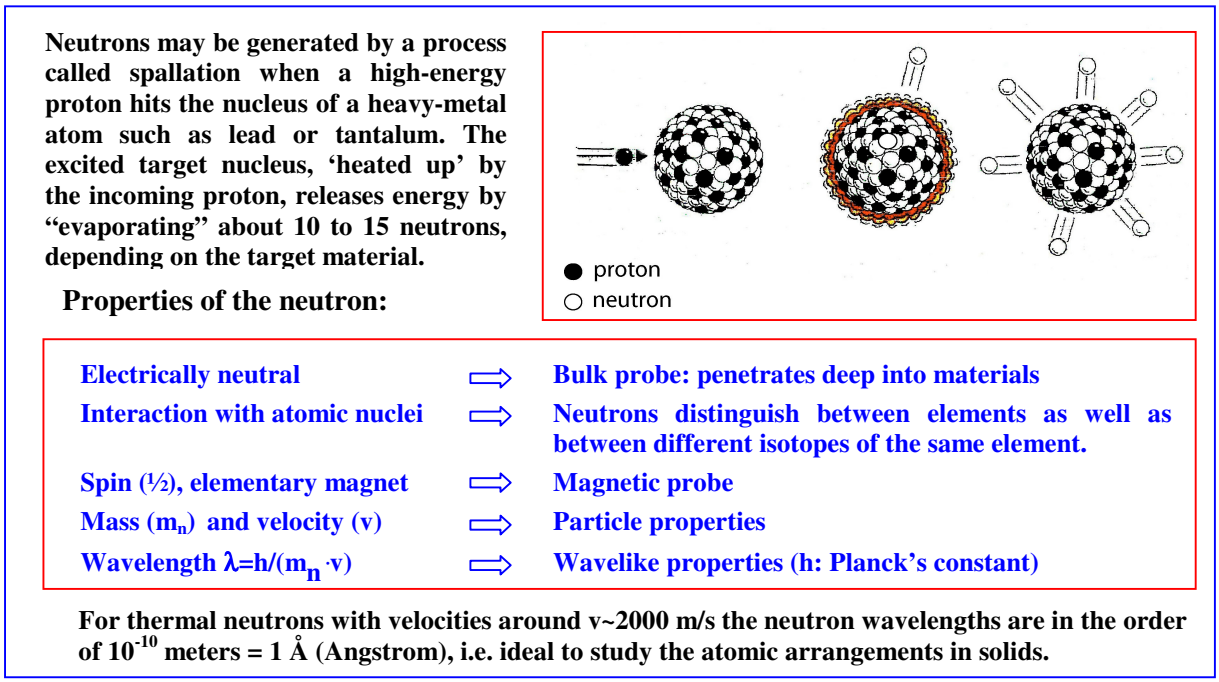


Fig. 1 *– Illustration of the spallation reaction and list of some of the neutron properties that are relevant for materials research (Brückel, 2001)]. Their high penetration capability makes neutrons a non-destructive probe. Moreover, they have just the right wavelengths to be used for diffraction experiments.*

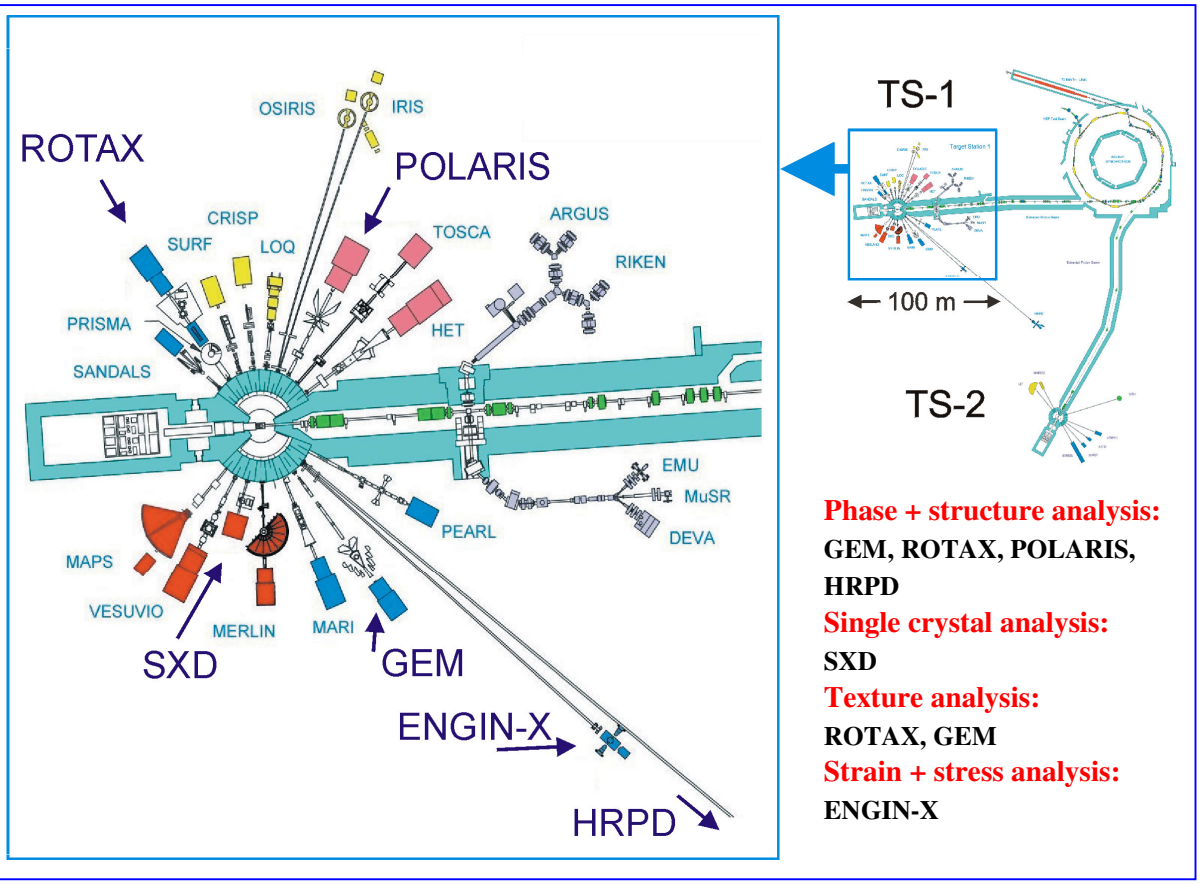


Fig.2 *– ISIS neutron spallation source*

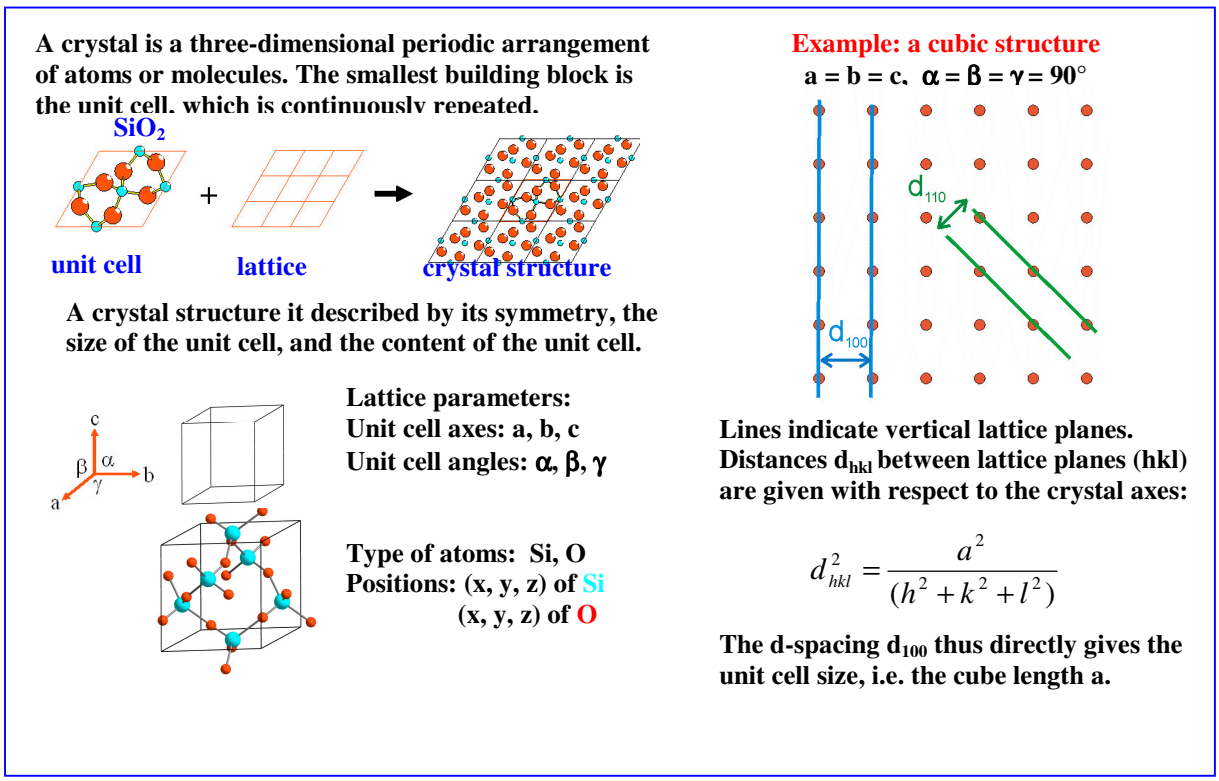


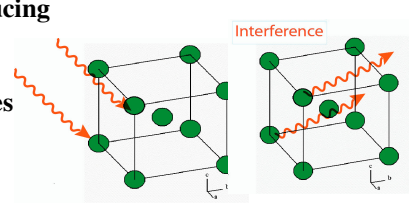
Fig.3 *- Description of a crystal structure*

The ISIS neutron spallation source at the Rutherford Appleton Laboratory in Oxfordshire is a large-scale facility, first of all because it operates a particle accelerator for getting the protons up to speed, secondly a huge experimental hall is required to house the massive shielding blocks and the suite of experimental stations (Fig. 2), thirdly ISIS is the most intense spallation source worldwide at the moment (ISIS Report 2003). A bunch of protons is accelerated in a synchrotron and directed towards the target station (TS-1) to produce neutrons in a composite tungsten/tantalum target. The high energy neutrons are slowed down in moderators in order to be useful for condensed matter studies before they are guided to the experimental stations, the "instruments". The neutron source generates 50 intense neutron pulses every second. This time structure is an important feature of the spallation source enabling instruments to efficiently use time-of-flight techniques. Fig. 2 shows the suite of instruments around TS-1. The diffraction instruments that are of special interest for archaeometric studies are highlighted. The second target station TS-2 is currently under construction.

3. Diffraction analysis

Archaeological materials often contain crystalline components such as minerals, multi-mineralic rock material, pure metals, alloys, corrosion products, or pigments. These materials have in common that they can be described by crystalline structures as regular and repeating arrangements of atoms (Fig. 3). The knowledge of the crystal structure of a material is of fundamental importance for understanding many of its physical and chemical properties and how it behaves under mechanical stresses or external environmental influences. Furthermore, the microscopic structure of a material often carries information about the mechanical deformation history. A crystal structure is specified by the chemical composition, the dimensions of the unit cell, and the atom positions within the cell. The study of periodic structures is the domain of crystallography where most concepts and applications are based on the knowledge of the symmetries of a crystal. For a known material the "space group" crystal symmetries, the lattice parameters and the atom positions can be taken from crystallographic data bases (PDF, JCPDS-ICDD; ICSD; CRYSTMET)). The symmetry of a crystal determines, among other things, the shape of the unit cell. The space group Fm3m, for instance, describes the well-known face-centred cubic (fcc) structures of many metals. In general, every crystalline material or "phase" has a unique crystal structure in terms of symmetry, lattice parameters and atom positions. Phases can be chemically identical but structurally different. For example, silicon oxide SiO_2 occurs in different structure modifications as quartz, cristobalite or glass.

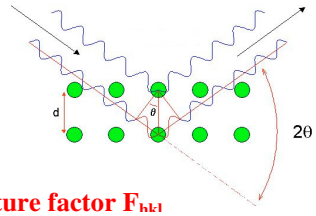
Neutron waves are deflected by atoms in a crystal. The scattered waves show destructive and constructive interference producing diffraction peaks at characteristic 2θ scattering angles between incoming and outgoing beam.



Bragg's law states that diffraction can be regarded as reflections of neutrons by crystal lattice planes.

Bragg's law:

$$2d_{hkl}\sin\theta = \lambda$$

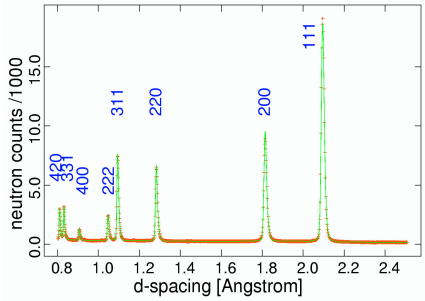


Intensity I_{hkl} <> structure factor F_{hkl}

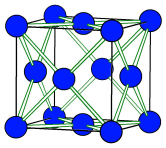
$$I_{hkl} \propto |F_{hkl}|^2 = \left|\sum_j b_j \cdot \exp\{-2\pi i(h \cdot x_j + k \cdot y_j + l \cdot z_j)\}\right|^2$$

d_{hkl}: d-spacing; 2θ: scattering angle; λ: wavelength
b: neutron scattering length; x,y,z: atom positions

Diffraction pattern from copper



The diffraction pattern allows to reconstruct the crystal structure, i.e. to derive the lattice constant and the atom sites from the positions and intensities of peaks, respectively. The presence or absence of reflections indicates the symmetries of the crystal.



space group: Fm3m
a=3.6145 Å
(x, y, z)=(0, 0, 0)

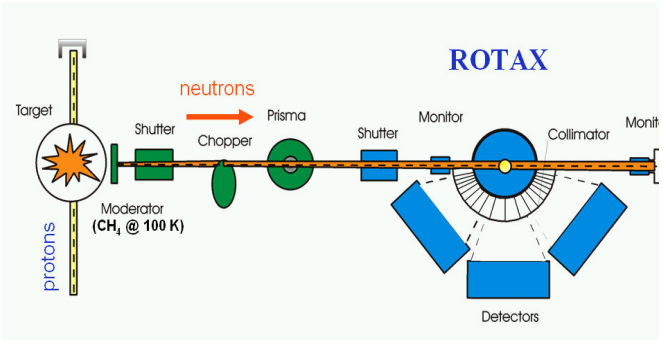
Fig.4 *- Diffraction from a crystal.*

Diffraction is ideal for studying any periodic arrangements such as atoms in a crystal. Diffraction is a general phenomenon that occurs if waves are impinging onto an obstacle, be they sound waves, light waves, X-rays or particle waves. Diffraction is based on the superposition of waves that re-enforce each other (constructive interference) or cancel each other out (destructive interference) (Fig. 4). Since the interatomic distances in a crystal are of the order of several Angstrom, X-rays and thermal neutrons are ideal for diffraction on crystals because they have just the right wavelengths. Intensity maxima occurring at characteristic scattering angles in the diffraction pattern are called "Bragg peaks" or "Bragg reflections" which are denoted by indices (hkl), where h, k, l can be any integer numbers. For example, (100), (010), (001) are the planes parallel to the faces of a cube but also denote corresponding peaks in the diffraction pattern. That is to say, each peak in the pattern corresponds to a family of parallel planes in the crystal. A crystal with a small unit cell and high symmetry, for example a cubic metal structure, produces a rather clear diffraction pattern with few peaks. In contrast, a complex structure with a large unit cell and low symmetry, for example a monoclinic feldspar mineral, has a complicated diffraction pattern with a large number of peaks. In general, every phase with a unique structure generates a unique diffraction pattern. Thus, the diffraction pattern can be regarded as a fingerprint of the crystal structure.

At this point it should be noted that most ceramic or metallic archaeological materials are poly-crystalline and multi-phase opposed to single-crystallline and single-phase, respectively.

The corresponding multi-phase diffraction pattern is composed of several single-phase patterns. Polycrystalline samples are made of a huge number of tiny single crystals ("crystallites") or grains, each of which may have a different size and orientation than its neighbours. Sometimes the grains may be oriented at random, then the material is said to be free of texture. If the grains may have preferred orientations from a particular mechanical treatment, then the material is said to exhibit texture.

Bragg's law offers two experimental methods of obtaining diffraction patterns. (1) In the angle-dispersive mode using a constant wavelength λ one obtains diffraction peaks at varying scattering angles 2θ depending on the distribution of the lattice plane spacings d_{hkl}. (2) In the energy-dispersive mode 'white' radiation with a broad range of wavelengths scattered at a fixed angle 2θ gives rise to a reflection whenever a combination of wavelength and d-spacing meets Bragg's law.



$$v = \frac{L}{t}$$ t: time-of-flight (example: 7 millisec); v: neutron velocity (2000 m/s); L: flight path (14 m)

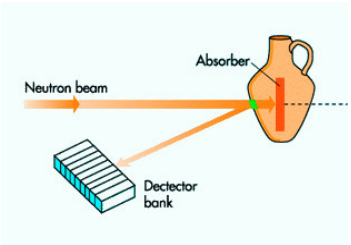
$$E = \frac{m_n \cdot v^2}{2}$$ E: neutron energy ($m_n = 1.675 \cdot 10^{-27}$ kg)

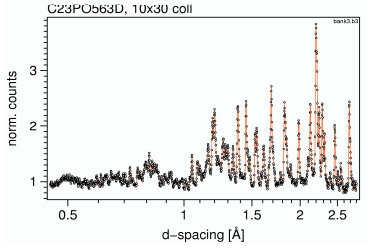
$$\lambda = \frac{h \cdot}{\sqrt{2 m_n E}}$$ λ: wavelength (2 Å) ($h = 6.626 \cdot 10^{-34}$ Js)

$$\lambda = 2d \cdot \sin\Theta$$ d: d-spacing (1.4 Å) ($2\theta = 90$ deg)

Neutrons produced in the target station are slowed down to thermal energies before they travel to the sample position at 14 meters from the moderator. About 1 million neutrons per second hit the sample at different speeds and wavelengths between 0.5 and 5 Å. The beam size ranges from 5x5 up to 20x40 mm. Neutrons, diffracted in the sample, are recorded by three neutron detector banks that measure both the 2θ angles and the flight times.

TOF-ND determines the flight time (t) of a neutron travelling from target to detector. With the flight path (L) known, one obtains the velocity, the energy, and the wavelength using de Broglie's relation. For a detector at a fixed 2θ angle, the d-spacing is derived from Bragg's law.





Left: A TOF-ND analysis is as simple as shown in the schematic. The neutron beam illuminates a stationary object. Neutrons penetrate into the interior of the vase's wall. Most of them pass through without interaction, only some neutrons are scattered and registered in the detector. A neutron absorber such as boron carbide may be used to stop the neutron beam inside the object. Alternatively, a radial collimator prevents neutrons scattered from the second wall from entering the detectors (see schematic at top). Middle: object inside the ROTAX sample tank, lying on a table. Right: The measured diffraction pattern displays normalized neutron count rates versus d-spacings.

Fig. 5 *- TOF-ND experimental set-up of the ROTAX diffractometer*

In both cases the intensities can be plotted versus the d-spacings using Bragg equation. The task of the diffraction analysis is to evaluate the measured diffraction pattern in terms of peak positions, peak widths and peak intensities. The peak positions are directly related to the crystal lattice dimensions. The Bragg peak intensities, however, are determined by the atomic arrangement in the unit cell, as given by the structure factor F_{hkl} (Fig. 4) which contains the neutron scattering lengths b_j (which atoms are present?) and the position coordinates (x, y, z) (where are the atoms?). The intensity distribution of the pattern is therefore characteristic of a known structure, or vice versa, the structure can be determined from the diffraction intensities.

The basic diffraction concepts are equally valid for X-rays and neutrons. The fundamental difference lies in the type of interaction with atoms and, consequently, (i) in the sensitivity of the two probes for elements and structures and (ii) in the absorption in matter. X-ray radiation with a comparatively low penetration depth of several tens of micrometers is well suited for studies on powders, small single crystals and surfaces. Neutrons with a large penetration depth in the order centimetres are well suited for bulk measurements on thick, intact objects.

4. Time-of-flight neutron diffraction (TOF-ND)

Fig. 5 shows the experimental set-up of the ROTAX diffractometer at ISIS. Diffractometers at a spallation source almost always use time-of-flight (TOF) measurements for determining the energies of the neutrons. TOF instruments are usually operated in angle- and energy-dispersive mode with detector banks at forward and backscattering 2θ angles. Each of the detector banks yields a TOF pattern that covers a certain range of d-spacings, as given by Bragg's equation for a given wavelength band and for a fixed 2θ detector angle. An important parameter of a neutron diffractometer is its resolution. It describes the instrumental contribution to the peak widths and depends on scattering angle, flight path, time-of-flight and sample thickness. TOF diffractometers have best resolution, i.e. sharpest diffraction peaks, at backscattering angles where, consequently, sample-related peak broadening effects are recognized first (Fig. 6). A good instrument resolution is required for peak separation in multi-phase sample patterns, for linewidth analyses, and for accurate determinations of lattice parameters.

Besides the general advantages of neutrons for material analysis, e.g. the non-destructive nature of the probe, there are several reasons to use a TOF neutron diffractometer for studying artefacts:

- The experimental set-up is mostly stationary and the shape of the object is less important since diffraction patterns can be collected at any detector angle, for example in backscattering.
- The diffraction peak widths at backscattering angles are practically independent on the sample thickness. Thus, sharp diffraction lines can be obtained, even from thick and bulky objects.
- All detector banks accumulate complete diffraction patterns at the same time, and from the very start of a measurement with best resolution. Hence collections times but also the neutron activation of the object in the neutron beam can be controlled and kept to a minimum.
- Robust crystal structure determinations are achieved due to partially overlapping d-spacing ranges and redundant diffraction information from different detectors banks.

It was demonstrated before that TOF-ND data collected from a large ceramic object and from a powder sample basically yield the same phase fractions (Kockelmann, 2001). For the data collection objects are positioned at the sample position and measured as they are. The only preparation required is to produce a safe object holder. Sometimes objects are wrapped in aluminium foil to record aluminium Bragg peaks as calibration markers. Data collection times are in the order of minutes up to hours depending on the size and complexity of the objects.

5. Information content in the neutron diffraction pattern

TOF diffractometers are automated to a large extent and are able to produce a massive amount of data within hours. The data analysis, however, can be intricate because the complexity of a multi-phase archaeological material is passed on to the diffraction diagram. The diffraction pattern of a pure metal with cubic symmetry may contain a rather small number of about 20 Bragg peaks. A multi-mineralic piece of pottery on the other hand may generate thousands of peaks. The task of diffraction analysis is to disentangle the different phase contributions and to extract structural parameters for the individual phases.

The structure of a polycrystalline material may be characterised at different levels (Bunge, 1999)

- The “phase structure” describes the composition of a material from several phases.
- The “crystal structure” deals with the atomic arrangement of each phase.
- The “grain structure” represents sizes, shapes and mutual orientations (texture) of grains.
- The “microstructure” describes structural deviations from an ideal crystal within a grain.

This classification is not clear-cut. In the literature, particle sizes and shapes are often referred to as microstructural properties rather than being part of the grain structure.

Sometime the term microstructure is used to refer to both, the grain and defect structure. The four structural levels are, of course, interdependent. For example, the change of the crystal structure by substitution of atoms may introduce microstrains. Also, the type and magnitude of microstrains introduced by mechanical deformation may depend on the initial texture. Cold working is expected to generate slipping of crystal planes, residual stresses and changes of the initial texture. Generally, direct evidence of working processes may be imprinted at one or more of the structural levels. Diffraction yields information on all four of them.

In the following the diffraction analysis is broken up into separate steps, knowing that also the data analysis steps are interdependent. For example, a reliable quantitative phase analysis depends on the knowledge of the texture of the material whilst texture analysis is made easier if the crystal structures of the phases are known. Some structural features can be identified and qualitatively interpreted just by close inspection of the diffraction patterns and by comparison to reference data (Fig. 6). A quantitative evaluation of the structural properties, however, requires set-up of theoretical models for analysis of the data in terms of peak positions (lattice parameter changes, macro- and microstrains), peak widths (particle size and microstrain broadening) and intensities (atom arrangements and grain orientations), ideally in a combined analysis (see Chateigner)

Changes of the grain structure and of the microstructure are often identified by close inspection of positions, widths and intensities of Bragg peaks. Comparisons with theoretical patterns or with diffraction data from control samples help to interprete the measured patterns. The peak position is given as d-spacing d [Å]. The peak width is given as full width at half maximum FWHM [Å]. The red curves display the instrumental peak widths as given by the diffractometer resolution.

Peak shifts may originate from (i) changes in alloy composition, e.g. incorporation of Sn in a Cu/Sn bronze (blue curves), (ii) (residual) macrostrains from material deformation.

Peak broadening may be attributed to:
(i) particle size broadening
(ii) distributions of lattice parameters in inhomogeneous alloys. A cast bronze, for instance, may display structured peaks due to irregular alloy composition variations (top blue curve).
(iii) microstrain broadening within crystallites after lamination or thermal treatment. The resulting distribution of lattice parameters around an average value may be smooth and narrow if slow annealing was involved in the working process (blue curve in the middle diagram) compared to a much broader distribution if the sample was quenched.

Peak intensity changes may indicate a change of the (i) phase mixture, (ii) crystal structure of one of the phases, or (iii) may be due to texture in the material (red+green curves, bottom), i.e. relative intensities depend on the sample orientation.

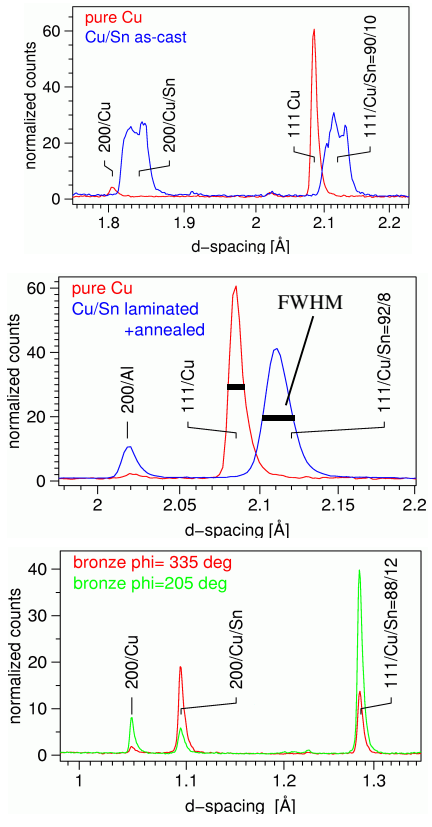
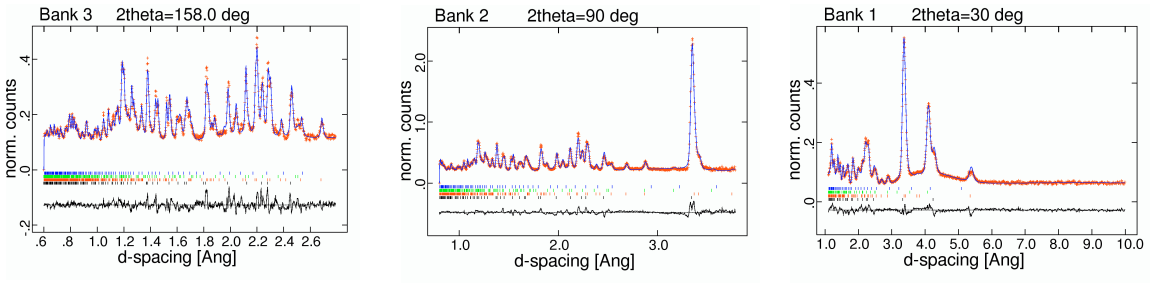


Fig. 6 *- Texture and microstructural effects on Bragg peaks.*

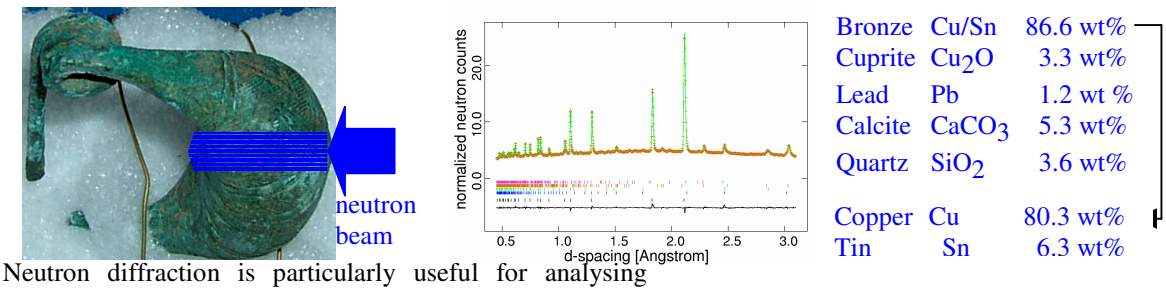


The diffraction patterns from a medieval stoneware shard cover different d-spacing ranges with different resolution corresponding to the three detector banks on ROTAX. For the quantitative analysis of the data standard crystallographic procedures are applied:

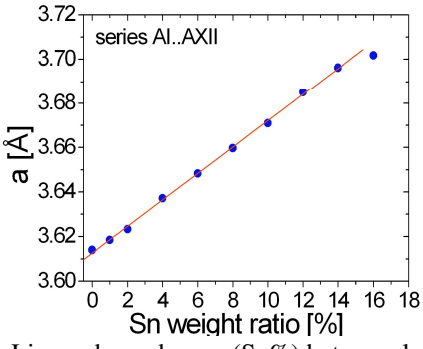
a. *Phase identification:* The Bragg reflections are indexed by assigning (hkl) of identified phases. Association of measured with calculated peak positions can be made using databases search-match routines such as PDF, ICSD, and CRYSTMET
b. The *crystal structure model* of a multi-phase mixture is composed using the single-phase structures (space group, lattice parameters, atom positions) for all identified phases according to their standard crystallographic description. The structure models are set-up using diffraction analysis software like GSAS, FULLPROF or MAUD all of which allow to calculate neutron diffraction patterns for any diffractometer geometry for comparison with observed patterns.
c. A *Rietveld analysis* is performed by least-squares fitting the calculated patterns to the observed diffraction patterns. This full-pattern fitting process permits to quantify the phase composition by adjusting the scaling factor for each single-phase component in the model. At the same step the structure parameters such as lattice parameters can be adjusted. This so-called multi-phase and multi-bank Rietveld refinement is performed with GSAS, FULLPROF or MAUD.
d. *Microstructural characterisation*: Most Rietveld programs allow for refinement of peak broadening parameters (microstructure) and preferred orientation parameters (texture).

The Rietveld fitted patterns above display the observed (red points), calculated (blue line) and difference (black line) diffraction patterns. There is a good agreement between observed and calculated patterns. The analysis reveals the presence of 33.1 wt% quartz (SiO_2), 30.9 wt% mullite ($3Al_2O_3{\cdot}2SiO_2$), 19.8 wt% cristobalite (SiO_2) and 16.2 wt% silica glass (SiO_2) in the pottery. The weight fractions add up to 100 wt%.

Fig.7 *- TOF-ND data analysis.*



Neutron diffraction is particularly useful for analysing closed objects with hidden material on the inside. A closed Etruscan fibula (National Archaeological Museum of Ancona, Italy) was illuminated on ROTAX (Siano, 2004) with a large neutron beam of 20x20 mm cross section. There is no information on the spatial distribution of the identified phases because all the material in the neutron path is illuminated. It is fair to assume that bronze, cuprite and lead are components of the fibula's shell, whereas calcite and quartz are part of the ceramic core. The tin content of the bronze is estimated from the lattice parameter shift with respect to pure copper, using calibration data from suitable bronze reference samples. This analysis assumes that the bronze contains only tin as alloying element



Linear dependence a(Sn%) between lattice parameters and tin content (Siano, 2003)

Fig.8 *- Combined phase and structure analysis of an etruscan fibula.*

5.1 Quantitative phase analysis

The multi-phase data analysis of archaeological samples involves identification of the crystalline phases and determination of the amount of each phase in the mixture. The quantitative analysis is based on the principles that (i) each phase exhibits a unique set of diffraction peaks, (ii) the intensities of each phase are proportional to the phase fraction, (iii) the measured diffraction pattern is the simple sum of all single-phase patterns. This means, a variation in the phase mixture only affects the relative Bragg intensities in the total pattern. An established method for the quantitative phase assessment is Rietveld analysis (Fig. 7) (Young, 1993) which yields phase fractions of the main phases.

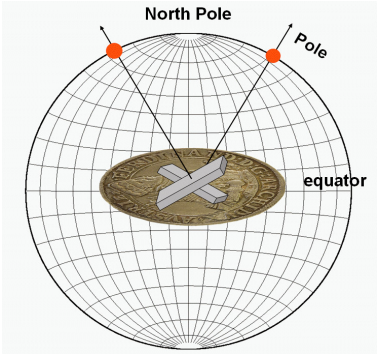
The presence and the absence of certain minerals in a piece of pottery, for example, and a quantitative assessment of the mineral mixture may provide information about the initial clay mixture and about firing temperatures and the firing atmosphere. Firing minerals like mullite or cristobalite are produced during drying and firing of the starting materials when the minerals undergo complicated transformations and phase transitions into new compounds that are critically dependent on the firing processes. This means that the mineral phase compositions of different ceramics are generally dissimilar, although the complexity of the phase transformations makes it almost impossible to reconstruct the firing processes in every detail.

TOF-ND achieves a truly quantitative analysis of the phase mixture from illumination of intact objects. The lack of an internal standard, however, means only relative phase weight fractions with respect to the crystalline portion of an object are obtained, ignoring non-crystalline and organic components. Nevertheless, ratios of phase fractions can be formed as useful quantitative indicators for characterisation and attribution purposes.

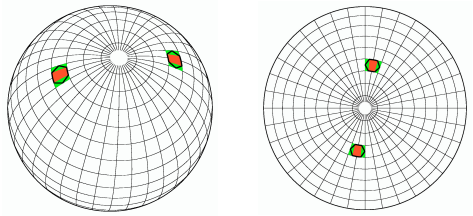
5.2 Crystal structure analysis

The diffraction peaks that belong to a particular phase are used to examine the crystal structure, i.e. the atomic arrangement of that phase. Neutrons also see the periodic order of atomic magnetic moments in magnetic minerals such as hematite or magnetite that are often present in archaeological objects. The information about the crystal and magnetic structures is related to both, positions and intensities of peaks. Fig. 8 shows an example of a combined quantitative phase and structure analysis. Crystal structure models, taken from data bases and included in the Rietveld analysis, can be adapted and refined. This is often done for lattice parameters because neutron diffraction can determine the lattice parameters of alloys and compounds with high precision. The cell constants of alloys (e.g. $Cu_{1-x}Sn_x$ bronze) often vary linearly in a wide composition range x according to Vegard's rule if smaller atoms (e.g. Cu) are replaced by bigger atoms (e.g. Sn). Neutrons are also able to detect structural changes such as exchanges of cations in minerals as the result of geophysical mechanisms.

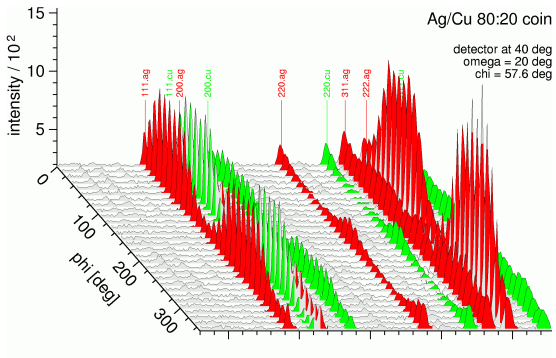
The crystal structure carries information on the preparation condition of a material because solidification and crystallisation from the melt critically depends on the thermal environment and treatment.



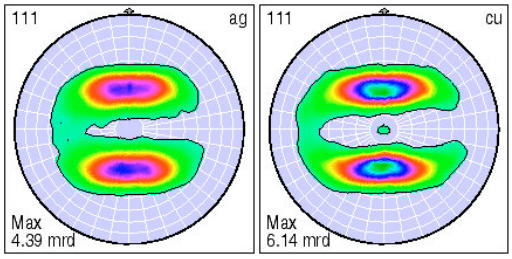
The object, here a coin, is considered to be inside an imaginary orientation sphere, the "pole sphere". The orientation of crystallites is represented by crystal planes and their "poles", the directions perpendicular to the planes.



Texture analysis determines how many crystallites are oriented in a certain direction with respect to the sample shape. A particular orientation is represented by a point on the pole sphere (left) and pole figure (right), respectively. A pole figure is the two-dimensional representation of the pole sphere.



For texture analysis the sample is rotated. One pattern is collected for each sample orientation angle (here phi). For every Bragg peak, the intensity variation as a function of sample rotation is entered into the pole figure of that peak.



It is important to note that texture analysis yields separate pole figures for each phase. The (111) pole figures of Cu and Ag are of the same type, indicating that the Ag/Cu alloy was cold-rolled in the same process. The colour code refers to multiples of a random distribution (mrd); mrd=1 denotes the average distribution.

Fig. 9 *- Texture analysis: pole figure collection.*

5.3 Texture analysis

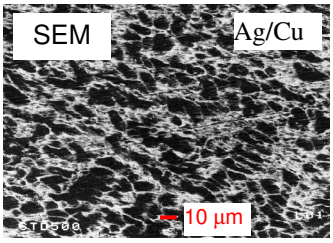
Neutron diffraction can be utilised to determine the orientation distribution of crystallites in a polycrystalline material. A polycrystal with a preferred orientation of crystallites is said to have texture (Schäfer, 2002). If the grains in an object are oriented at random and if all grain orientations are equally realised then the material is said to be free of texture. Texture is an important material characteristic of metals, alloys and ceramics. It is the result of the solidification and manufacturing process and thus texture contains detailed information about the production history of a work piece (Kocks, 1998) Well defined textures are produced by specific conditions during primary crystallisation from a melt, and by thermal and mechanical

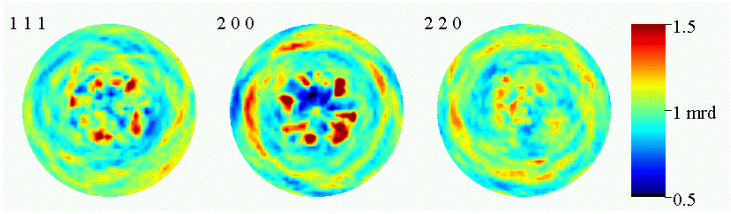
treatments of the cast such as annealing, drawing, rolling, and hammering. Neutron diffraction can therefore provide information on the creation and deformation history of an object, be it a modern engineering component, a mechanically deformed workpiece of archaeological interest or a geological sample deformed by tectonic processes.

Neutron texture analysis is an elegant method to determine the orientations of grains in an object. The presence of texture manifests itself as intensity variation of each Bragg peak as a function of the detector angle (Fig. 9). This orientation dependence of intensities originates from two experimental conditions: (i) crystallites have to be oriented according to Bragg's equation in order for a particular (hkl) peak to be recorded in the detector (ii) the measured Bragg intensity depends on the number of grains that meet Bragg's law. For a texture-free material the detector position does not matter because the number of contributing grains is always the same in contrast to a material with texture. The grain orientation distribution can be measured by recording diffraction patterns from many different angles (1) by rotating the sample or (2) by moving or building a detector around the sample. The first option is the classical texture set-up where a sample is mounted on a goniometer in order to realize a multitude of orientations. Owing to the high penetration power of neutrons and to the large beam sizes in neutron diffraction, textures with high grain statistics and grain sizes up to millimetres can be achieved, even for course-grained materials.

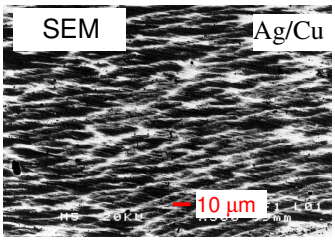
The texture information is displayed in so-called pole figures (Fig. 9). The pole figures are the maps of the grain distribution and, as such, are fingerprints of the historic making techniques. In case the methods of production are known, the pole figures can be used as signatures to distinguish genuine from fake objects (Fig. 10).

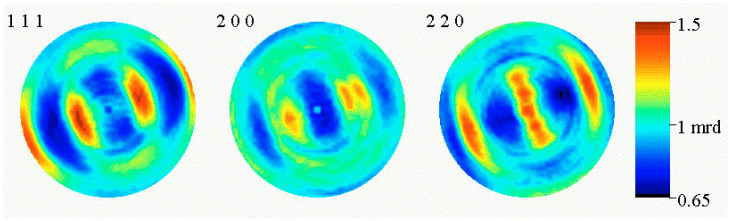
The texture analysis is also beneficial for the quantitative phase and crystal structure analyses that both require texture-free data sets. Diffraction data collected at different angles can be summed up in order to obtain an average quasi-texture-free diffraction pattern which can be analysed with the Rietveld method. In a different approach the texture can be modelled and accounted for in a combined phase-structure-texture analysis. Program like GSAS (see Ref) and MAUD (see Ref.) can be used for combined structure and texture refinement yielding weight fractions, structure parameters and pole figures.





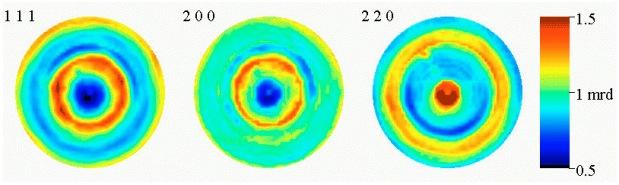
Cu pole figures, as-cast



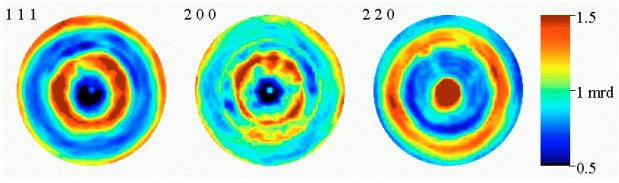


Cu pole figures, cold-rolled

Ag/Cu coin, Coin cabinet, KHM Vienna



96 % Ag



4 % Cu

Preferential alignment of crystallites in a material is often related to working processes. Pole figures display characteristic, irregular or regular, crystallite orientation distributions and are therefore fingerprints of the working technique itself. Whereas the direct SEM imaging requires cleaning and etching of the sample's surface, the texture determination by TOF-ND is done on the undisturbed object. Neutron diffraction on a silver coin from the Kunsthistorisches Museum Wien (Kockelmann, 2003; Schreiner, 2004) reveals circular pole density maxima of a fiber texture that clearly points to the minting process by striking with a hammer and a die.

Fig.10 *- Neutron texture analysis.*

5.4 Microtructure analysis

The widths of Bragg reflections may vary for different samples and even for different phases of one and the same sample. Peak broadening generally indicates deviations from ideal structures within crystallites in terms of size and defects (Bunge, 1999; Chateigner]:

- Particle size broadening is caused by the average size of the crystallites: the smaller the grain, the broader are the diffraction peaks. Large crystallites do not contribute to the broadening. Small crystallites (typically < 1 µm) cause broadening reflecting the finite size of the crystallite, i.e. the limited number of atoms that participate in the diffraction process.

- Microstrain broadening is caused by defects within a crystallite or grain. Lattice distortions and deformations that originate from missing atoms or extra impurity atoms in an otherwise ideal crystal may be responsible for microstrains that lead to a spread of lattice planes distances. Defects, lattice deformations and microstrains are also induced by mechanical and thermal working processes.
- A variation of the sample composition in the illuminated diffraction volume may cause peak broadening similar to microstrain broadening. For a very inhomogeneous material the spread of lattice parameters may even lead to markedly structured peak profiles (Fig. 6).

Slow heating and „annealing“ at high temperatures may reduce crystal defects and relieve lattice strains whereas a rough treatment like hammering and quenching in water generates microstrains. A peak broadening analysis can provide valuable clues to the working processes. Such an analysis is particularly useful if microstructural trends are revealed by comparison with suitable reference samples that are produced in a controlled way. It should be noted, however, that a linewidth analysis often gives ambiguous results and that there is not a one-to-one correspondence between linewidth and mechanical treatment. Different working cycles can lead to a simular type of broadening. Also, microstrain broadening and broadening due to compositional variations are difficult to distinguish. The analysis of the microstructure is even more complicated if different sources of broadening occur simultaneously. Particle size and microstrain effects can be evaluated and separated using mathematical approaches based on the Scherrer formula and the Williamson-Hall plot (Young, 1993). Peak broadening can be assessed by single peak FWHM analysis of individual Bragg peaks or as part of the full-pattern Rietveld analysis. In both cases the peak broadening by the diffractometer, the instrumental resolution, is taken into account. The linewidth analysis can be performed for each phase separately.

5.4 Residual strain-stress analysis

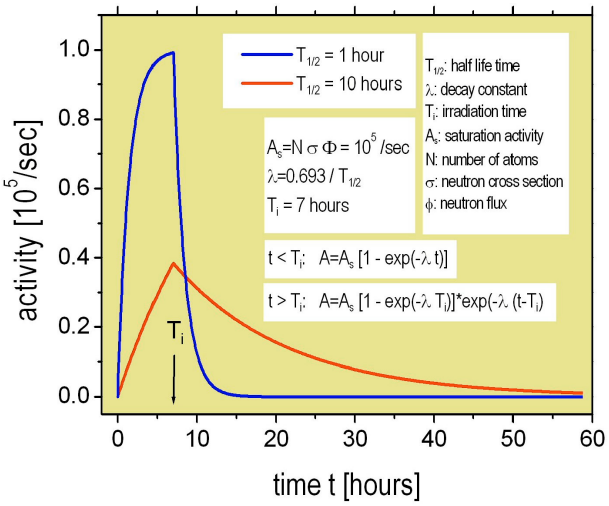
Residual strain measurements are very important in engineering sciences for non-destructive materials testing and quality control. The same technique can be applied to archaeological objects. Residual strains (or macrostrains) are induced by macroscopic compressive or tensile stresses as the result of working processes. The residual strains measured by diffraction represent the average strains within the irradiated sample volume. In contrast to the microstrains that lead to peak broadening, the residual strains cause shifts of Bragg peaks relative to their unstrained peak positions. For residual strain analyses it is essential to have the means to clearly define the illuminated volume in the sample and to collect diffraction patterns from orthogonal directions (see Fig. 12). Residual strain analysis of archaeological objects is a very new field and has only been attempted recently (Siano, 2003)

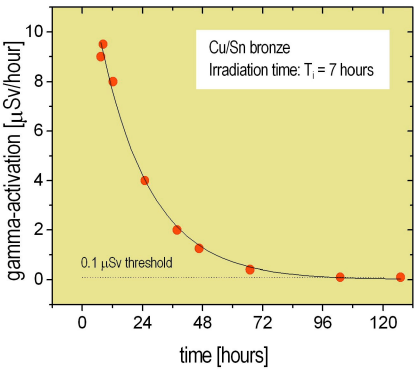
6. Advantages and Limitations

TOF-ND is used for material analysis in terms of crystalline phases, crystal structures and microstructures if sampling from an artefact is out of question. Compared to other phase and structure sensitive methods, like X-ray and electron diffraction, TOF-ND has the following advantages for archaeometric studies:

- The interior of intact and original objects can be examined non-destructively. The method is particularly useful to look through coatings and corrosion layers into the bulk of artefacts to identify hidden materials.
- Neutrons provide averaged and representative structural information from the inner parts of bulky objects avoiding problems associated with single-spot analyses.

When neutrons pass through matter, some of them interact with the atoms and generate *radio-nuclides or radio-isotopes, i.e.* unstable nuclei with a certain number of protons and neutrons. That is to say, the material which is in the neutron beam for a certain irradiation time (T_i) is activated for some time. The unstable nuclides transform into stable nuclei by radioactive decay through the release of alpha, beta, and/or gamma radiation. The number of particles emitted may be measured with radiation monitors as a function of time (t) in order to assess the *activity* (A) of the material in terms of counts/sec (becquerel) or the *equivalent dose* in micro-Sievert/hour. The time for the activity of a radio-nuclide to fall to half of its original value is called the half-life $T_{1/2}$.





In successive half-lifes, the activity of a material is reduced by decay to 1/2, 1/4, 1/8 etc. This means that one can predict how long it takes for the activation to drop to an irrelevant value. The limit for materials to be regarded as 'clean' at ISIS is 0.1 μSv/hour.
The top figure makes evident that a material with a short $T_{1/2}$ (e.g. Pb) is easily activated; however, it looses its activation quickly. On the other hand, a material with long $T_{1/2}$ (e.g. Cu) is more difficult to activate whilst it takes more time for the decay. The figure on the left shows the measured decay curve of a Cu/Sn sample (Siano, 2002) for which the activation disappeared after 3 days.

Fig. 11 *- Activation in the neutron beam.*

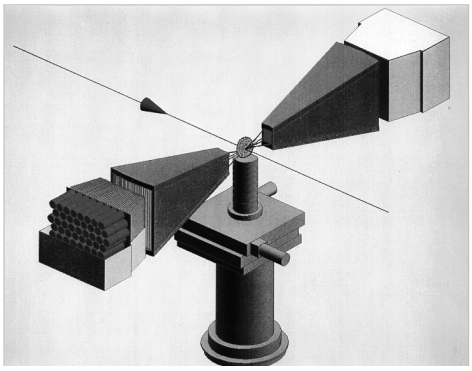
- The phase and structure analyses are truly quantitative by using rigorous constraints in terms of crystal structure models in the Rietveld refinements. The diffraction data analysis is not compromised by absorption or by graininess of the sample.
- Neutron texture analysis allows for the non-destructive mapping of grain orientations in the bulk in form of pole figures.
- There is no radiation damage induced by thermal neutrons.

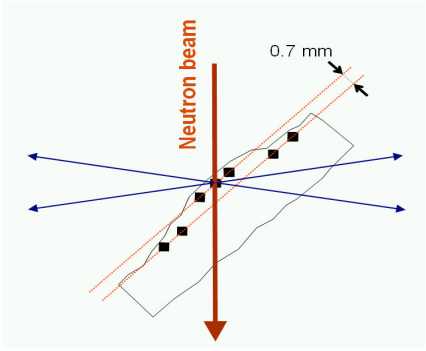
The actual TOF-ND experiment is rather basic and the information obtained refers to mainly average material properties. The main limitations of TOF-ND are:

- There is limited elemental sensitivity. Diffraction is basically phase sensitive.
- The phase analysis concerns only major phases down to a 0.2 weight percent level.
- The texture analysis often remains semi-quantitative if an object of awkward shape is difficult to manoeuvre and rotate on a goniometer for pole figure collections.
- TOF-ND lacks spatial resolution. Diffraction volumes are rather big (in the order of mm^3) compared to micro-diffraction applications at synchrotron sources (see http://srs.dl.ac.uk/arch/index.htm).
- In addition, there are some further drawbacks of TOF-ND:
- Objects have to be brought to the neutron source.
- Objects are radio-activated in the neutron beam for a certain time.
- The method is unsuitable for large sample series. The diffraction data analysis is hardly automated and has to be carried out sample after sample and data set by data set.

The activation of artefacts in the neutron beam is generally not a severe problem. However, one has to allow time for the induced activation to decay after the experiment. It is therefore important to limit the irradiation times in order to keep the activation decay times as short as possible (Fig. 11). The activation levels can be controlled (i) by restricting the irradiation times to a few hours, and (ii) by minimizing the irradiated sample volume. For ceramics the activation usually decays within minutes. Some elements like silver and copper have relatively long half-life times and it takes about 2 days for the activation to completely disappear.

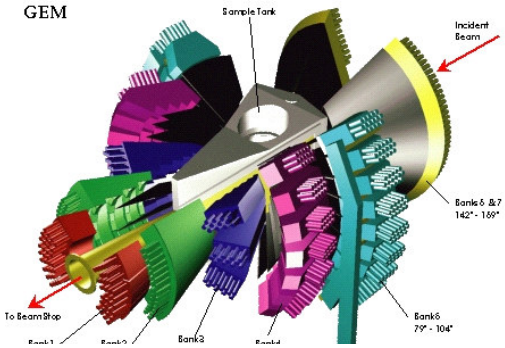
Residual stress and phase mapping on ENGIN-X at ISIS

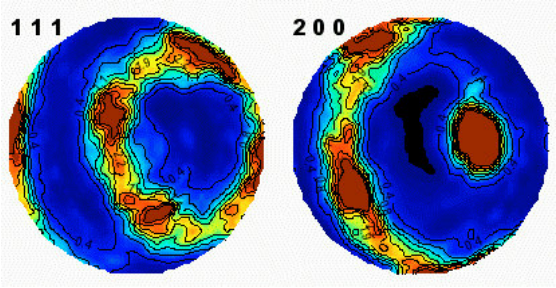




Scanning of a Roman coin along the surface to map the residual stress profile (Siano, 2003)

Pole figure collections on GEM at ISIS





Pole figures collected on a fiber-textured Cu sample without sample rotations on GEM (Artioli, private communication)

Fig.12 *- Advanced TOF-ND instruments for archaeometry.*

7. Future prospects

A rather broad neutron beam, usually several centimetres in diameter, probes a large volume portion of the object to obtain representative and statistically meaningful structural information. This experimental procedure, however, lacks spatial resolution. In order to fully exploit the potential of TOF-ND high spatial-resolution scanning capabilities of neutron strain scanners, such as ENGIN-X at ISIS, need to be used. First pilot experiments on ENGIN-X for characterising archaeological objects have been performed recently (Siano, 2003) (Fig. 12). ENGIN-X achieves spatial resolution (i) in diffraction mode by using narrow collimators for the incoming and diffracted neutrons and (ii) in transmission mode by using a large incoming neutron beam and a pixellated detector behind the sample in a radiography-type set-up. Both experimental set-ups allow to obtain maps of Bragg peak positions and, consequently, yield accurate mappings of lattice parameters and residual strain distributions in the bulk of an object. Moreover, since the diffraction mode is capable of scanning a diffraction volume of

5×0.5×0.5 mm along any path across the object, one can consider to produce three-dimensional maps in tomographic-type experiments in terms of phase composition and microstructure. The ability to combine the spatial resolution with phase and structure information constitutes a powerful tool to look into solid archaeological objects.

Another promising development concerns the use of GEM type instruments for texture analysis. GEM has about 6500 individual detectors, grouped into six detector banks, installed around the sample position. The large detector coverage allows to collect pole figures with just a few sample orientations. In some cases no sample rotations are required and complete texture data can be collected within minutes. Pole figures collected in a single-shot acquisition on GEM on a stationary copper sample are shown in Fig. 12.

8. Conclusions

Neutron diffraction is a non-destructive diagnostic tool for analysing the structures of materials at an atomic level. The method is capable of extracting essential microstructural data from the interior of undisturbed artefacts using existing instrumentation and basic crystallographic tools. By illuminating a considerable volume portion of an object, neutron diffraction provides overall and average information on the phase abundance, on the arrangements of atoms (crystal structures) and arrangements of grains (texture) as well as on macro- and microstrains in the bulk material. The structural characterisation permits to reconstruct details of the making techniques and deformation history, which is key information for addressing: (1) attribution and authentication of an object, (2) ancient materials and ancient technologies, and to a lesser extent (3) conservation issues such as the assessment of the corrosion state and stability of an artefact.

Neutrons are powerful probes for fundamental condensed matter research but also for testing of engineering components and archaeological objects. Finally it should be noted that large scale facilities usually make neutron beams available for all interested groups from universities and research institutions. Beamtime is normally allocated, free of charge, on request through a proposal and peer review system.

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