

forming oxo-bridges between the metal ions are identified, and four water molecules are found to be associated with the metal cluster, some of which may serve as substrates in the oxygen-evolving reaction. The most significant structural feature of the Mn4Ca-cluster is its distorted chair form. The large distortion from a symmetric cubane is principally caused by the existence of Ca and O5, the fifth oxo-bridge connecting three Mn ions and one Ca ion. The distances between the four metal ions and O5 are remarkably longer than those between the other oxygen and metal ions. This suggests that the bonds between O5 and each of the Mn and Ca ions are very weak, implying that O5 is apparently different from the other four oxygen atoms and may therefore have a higher reactivity. It may also suggest that O5 has a lower negative charge compared with a valence of -2 expected for normal oxygen atoms in oxo-bridges, which in turn suggests that O5 may exist as a hydroxide ion in the S1-state of the Kok cycle.

In order to elucidate the mechanism of PSII oxygen evolution, it is crucial to identify the two substrate-water molecules participating in the O-O bond formation. Based on the above structural features revealed, O5 may form part of the reaction site. Among the four water molecules bound to the Mn4Ca-cluster, two are located most closely to O5, with their distances to O5 around 3 Å. In addition, these two water molecules have a distance of 3.3 Å between each other. Thus, it is most probable that O-O bond formation is taken place within these two water molecules and O5. In the conference, based on the crystal structure precisely determined at the resolution of 1.9 Å, we will propose two types of oxygen evolution mechanism. One includes O5 and one of the four water molecules bound to the Mn4Ca-cluster as the substrates of oxygen evolution reaction, whereas the other one does not include O5 and assumes that the O-O bond formation is taken place within two of the four water molecules.

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Keywords: oxygen evolution, photosynthesis, photosystem II

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Rietveld refinement using G-Faktor applied on early OPC hydration

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The quantitative phase analysis during early hydration (24h) of Ordinary Portland Cement (OPC) is challenging due to the presence of variable amounts of different amorphous phases and water [1]. For some phases which are crystalline like monosulphate 14-hydrate structural data are not available. Classical use of Rietveld refinement does not deal with that challenge because the calculation of fitted phases is always normalized to 100 wt.-%. The use of an internal standard is not appropriate due to the known filler effect on the hydration of the OPC. Therefore a remastered external standard method using the G-factor can be employed [2]. We made use of Silicon as an external standard material. The G-factor can be derived from equation 1:

$$\text{Eq. 1} \quad G = s_{\text{Si}} \frac{\rho_{\text{Si}} V_{\text{Si}}^2 \mu_{\text{Si}}^*}{c_{\text{Si}}} \quad \text{with:}$$

s_{Si} = Rietveld scale factor of silicon
 ρ_{Si} = Density of silicon

V_{Si} = Unit-cell volume of silicon
 c_{Si} = Silicon content(100 wt.-%)
 μ_{Si}^* = Mass attenuation coefficient (MAC) of silicon

By determination of that G-factor any single phase might now be calculated from the equation 2 [3]:

$$\text{Eq. 2} \quad c_j = s_j \frac{\rho_j V_j^2 \mu_{\text{SAMPLE}}^*}{G}$$

Data needed can be extracted from Rietveld results. Only the μ_{SAMPLE}^* has to be calculated from the chemical composition which was determined in our investigation by XRF of the dry cement and the amount of mix water. Using that technique we followed the hydration reaction of OPC during the first 24h after contact with water. The quantitative data show an enormous accuracy with errors smaller than 0.1 wt.-% within one preparation. Main advantage of the method is the independent phase determination of any phase without normalization to 100 wt.-%. These accurate phase content was compared to the heat evolution of the cement measured by isothermal calorimetry. The multiple heat flow events in the pattern could be assigned with the help of the quantitative phase evolution. In a next step heat flow (HF) patterns were calculated from the quantitative phase data using equation 3.

$$\text{Eq. 3} \quad HF = \frac{\partial \text{wt.-% phase}}{\partial t} \times \Delta HR \quad \text{with}$$

$$\frac{\partial \text{wt.-% phase}}{\partial t} = \text{Derivative of the phase content from G-factor}$$

$$\Delta H_R = \text{Enthalpy of reaction}$$

Heat flow calculated from the change of phase content during hydration time determined by G-factor analyses fit very well the measured heat flow curves.

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Keywords: rietveld, cement, hydration

MS.32.2

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Materials development; novel applications of time-resolved diffraction

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For almost a decade the development of ultra-fast, high-flux diffractometers has largely exceeded the experimental requirements of most users. Fortunately, in recent years the unique capabilities of these instruments have become more widely recognised and they are being applied as a reliable means of analysis. When combined with position sensitive detectors (PSDs) capable of a wide angular range (5-160° 2θ) and very fine time-resolution (<100ms), high-flux diffractometers begin to emerge as an industrially relevant technique in the design, characterisation and certification of advanced materials. The ability to implement such detailed analysis has been significantly aided through the concurrent development of batch Rietveld data processing suites and the Quantitative Phase Analysis (QPA) technique.

This present research will outline developmental work using the D20 diffractometer (ILL, France) in the exploration of a case study; *M_{n+1}A_xN Phases*. D20 has enabled us to explore the ultra-fast reaction kinetics of a Self-propagating High-temperature Synthesis (SHS) of

model $M_{n+1}AX_n$ Phase systems at a <100ms time resolution. In turn, this technique has been further refined and applied in the confirmation of a novel solid state $M_{n+1}AX_n$ Phase precursor design. The ability to simultaneously explore the *in situ* chemical and thermal environments of large volume samples has provided us with a means of rapidly prototyping novel synthesis techniques. More generally, time-resolved *in-situ* neutron diffraction has the potential to redefine many research techniques in both materials science and solids state physics if two experimental methodologies can be perfected; (i) concurrent experimentation and (ii) complementary analysis. More specifically, we should aim to couple *in situ* scattering with the simultaneous analysis of chemical, thermal, physical or environmental factors, while analysis using complementary techniques (e.g. neutrons & X-rays) will ideally produce higher scientific standards in characterisation. Together, these methodologies significantly reduce the development time and complexity of novel materials syntheses, while ultimately lowering associated costs. The key to achieving these goals is the design and implementation of robust *in situ* sample environments capable of exploring a wide range of simulated service environments.

Keywords: *in situ*, diffraction, QPA

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Nonlinearity in residual stress measurements using X-ray powder diffraction

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Residual stress has often a strong influence on material properties, such as fatigue and stress corrosion resistance. X-ray powder diffraction can be used to measure the residual stresses in polycrystalline materials. Normally, the classic $d\text{-sin}^2\psi$ method is used to derive the stress from diffraction data [1]. However, it often happens that the $d\text{-sin}^2\psi$ data shows nonlinearity, either as oscillation (Fig. 1) or curvature (Fig. 2) for industrial materials (e.g. ferritic steel). The nonlinearity has been attributed to elastic anisotropy due to strong texture (Fig. 1) and stress gradients in the sample normal direction (Fig. 2), respectively [2]. Despite texture, d vs. $\text{sin}^2\psi$ linear relationships are still found for biaxial stress states for cubic materials in the case where elastic models apply, when $\{h00\}$ or $\{hhh\}$ planes are used for the stress measurement. The $d\text{-sin}^2\psi$ function is principally linear as long as only influences of texture in connection with residual stresses are present [2]. In the case of curvature due to a strong stress gradient, grazing incidence X-ray diffraction can be applied in order to reduce the penetration depth, therefore, $\Delta z \rightarrow 0$. Thus, the stress gradient would be zero. A linear $d\text{-sin}^2\psi$ plot is shown in Fig. 3 with 10° grazing incidence angle for the ferrite (200) reflection. However, in this case the measured stress is only the very surface stress. In order to obtain the stress gradient a series of measurements with varied grazing incidence angles should be carried out and the residual stress as function of sample depth could be obtained as shown in Fig. 4. In this way the nonlinearity in residual stress measurement using X-ray powder diffraction can be avoided.

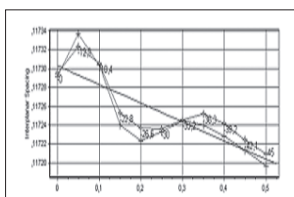


Fig. 1a. Oscillation $d\text{-sin}^2\psi$ plot using ferrite (211) reflection due to texture.

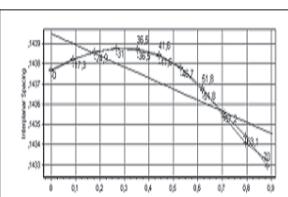


Fig. 2a. Curvature $d\text{-sin}^2\psi$ plot due to stress gradients in the sample normal direction.

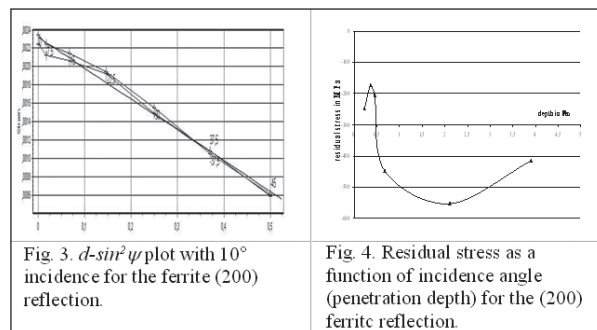


Fig. 3. $d\text{-sin}^2\psi$ plot with 10° incidence for the ferrite (200) reflection.

Fig. 4. Residual stress as a function of incidence angle (penetration depth) for the (200) ferrite reflection.

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Keywords: residual stress, X-ray powder diffraction, material sciences

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The development of rapid tomographic energy dispersive diffraction imaging TEDDI

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Energy dispersive diffraction has been shown to be useful in producing three dimensional X-ray images of objects where each voxel within the image contains structural information [1]. This coherently scattered signal can be used to identify the material concerned or to display some feature of the sample such as a chemical change or a stress distribution. A major difficulty with attempting to produce an image with weak diffracted signals is the slowness of the method. This has been partially overcome at lower energies by producing energy sensitive pixilated detectors combined with suitable collimator arrays to eliminate unwanted scatter and to define energy resolution [2].

However the vast majority of samples we wish to image for security scanning, aerospace or chemical engineering applications require much higher energy radiation for sample penetration. This requires high energy X-ray pixilated detectors and associated high performance collimators. We describe in this paper the development of an 80 x 80 pixilated array made from CdZnTe material and its application to the non-destructive study of the internal strain distribution in Ti6246 which is a superalloy widely used in the aerospace industry. We will also present the study of the evolution of an alumina catalyst support as function of processing [3].

We conclude that TEDDI, as one of the growing family of X-ray imaging methods, can deliver signals with suitable signal-to-noise in an acceptable timescale for scale-up to industrial applications.

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