Condensed Matter Physics

The Condensed Matter Physics Group is one of the groups contributing to the commonwealth of know-how and material resources of ITN oriented towards the development and characterisation of new materials based on a better understanding of condensed matter systems in general.

The local availability of important scientific and technical infrastructures, like the research reactor, the Van de Graaff accelerator and workshops, implanted in the campus many years ago, stimulated the build-up of teams of experimentalists and the acquisition of technical expertise in key areas related to the use of radiation as a tool to investigate material systems among other applications.

For historical reasons neutron scattering work has had and keeps a special place in the group's activities which is not unrelated to the perception of its importance for improving the utilisation of the nuclear reactor and developing a user community in the country and also for its potential as a tool for training young students. It is, in fact, a strategic aim to build up and operate routinely an infrastructure for neutron beam work at the RPI research reactor that can be used in research and for graduate and post-graduate training. This will be beneficial to a number of national groups, mainly in universities, and to the development of scientific exchanges with foreign scientists and institutions.

In this context, two new neutron instruments are expected to become operational during 2000: the Small Angle Neutron Scattering Instrument EPA, to be installed at the reactor tangential beam tube, and the 2-axis Neutron Diffractometer DIDE equipped with a 800-wire "banana" multidetector and a focusing crystal monochromator of pyrolitic graphite. Commissioning of the two instruments was originally foreseen to take place before the end of 1999. Due to various reasons this is now expected to occur between middle 2000 and the end of the year.

DIDE will be primarily used for the determination of magnetic structures of intermetallic compounds matching the local capacity of sample preparation. The research areas in view for the SANS instrument are the study of polymer gels and silica-based purely inorganic and organic-inorganic hybrid systems leading to vitreous materials of potential technological interest.

In recent years a considerable effort was made to broaden the group's capabilities by setting up a new laboratory centered on a *high resolution X-ray diffractometer* – the Hotbird.

The construction and furnishing of the new laboratory is now essentially complete.

X-ray diffraction measurements at high temperature, particularly, on single crystalline samples, are very useful and also very rare. The Hotbird, now in operation, is intended to study high temperature phenomena in *superalloys,* ceramics and semiconductors, and to measure residual stresses. The Hotbird allows carrying out locally highly specialised experiments that will impart substance to collaborations with foreign teams and the training of young scientists.

A relevant part of the group's activity concerns instrument development and optimisation as reported. In this respect the most important results obtained regard the optimisation of small angle neutron scattering instruments and, in special cases, of neutron and X-ray diffractometers.

Several joint research projects are currently under way in partnership with groups in and outside the country as reported. Neutron beam time is used regularly at the ORPHEE reactor in Saclay and occasionally at the British spallation source ISIS. Co-operation with the Institute for Advanced Materials, JRC, Petten, and the Lisbon School of Engineering (IST) in the field of high temperature structural materials continues. Co-operation in the field of SANS applications continues with Aveiro University (silica gels) and again with IST (aqueous ionic solutions).

The neutron time-of-flight diffractometer ETV, primarily intended for training and educational purposes, was utilised in demonstration experiments included in lectures for undergraduate students introductory to neutron scattering (collaboration with: Physics Dept., Faculty of Sciences, Lisbon University; IST, Technical University of Lisbon; and Physics Dept., Aveiro University).

Microstructure investigation of organic-inorganic hybrid materials*

F.M.A. Margaça, A.N. Falcão, J.S. Sousa[1], I.M.M. Salvado[2],
A.M.R. Mendonça[1] and F.G. Carvalho

Objectives

Preparation and characterisation of materials with an inorganic constituent composition of (100-x)SiO2.xMO2 (M=Ti, Zr) covalently linked with an organic component of polymeric material such as PDMS, to carry out a systematic investigation of the hybrids so obtained in order to find the dominant relationships between microstructure (mainly at the nanoscale), macroscopic properties and processing conditions. Particular focus will be placed on the influence of parameter x, polymer concentration and molecular weight and processing conditions.

Results

The project started in the second quarter of 1999. The first task planned was the preparation of hybrid materials, testing different preparation procedures, aiming ultimately at achieving reproducibility. This has been done for samples with one inorganic component (x=0). The alkoxides method of the sol-gel process that leads to high purity products at relatively low temperatures via hydrolysis and condensation of the appropriate alkoxides was used in the sample preparation. Several samples have been produced with systematic variation of processing conditions, using different PDMS concentrations and molecular weights and two different PDMS solvents.

The thickness of the wet gel poured into the sample container was found to be quite important to prevent mechanical failure of dried gels. All samples showed similar density, the majority being transparent. Mechanical properties varied from stiff to elastomer-like behavior, depending on the PDMS concentration and sample thickness.

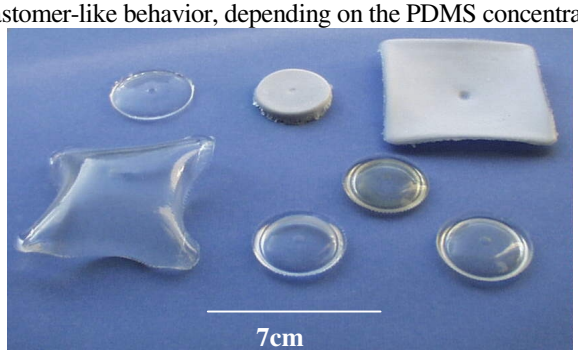

Fig.1 – Samples of organically modified silica. Samples are flexible, particularly, thin ones.

A preliminary nanostructure investigation has been performed using Small Angle Neutron Scattering, SANS, at Laboratoire Léon-Brillouin, just before Christmas of 1999. Data are still being analysed. However it is clear that deuteration (hydrogen isotopic substitution) of the polymer is necessary in future measurements.

Test measurements on the samples prepared at Aveiro and Sacavém could not be carried out using the EPA spectrometer facility, to be installed at the local RPI reactor, contrary to what had been originally planned. The fact that EPA is still not operational constitutes a serious drawback for the project for one is forced to adapt to the schedule for using beam-time set by Laboratoire Léon Brillouin (LLB), normally limited to one annual short beam time period [1] and consume part of it carrying out test measurements of untested samples.

References

1. Falcão. A.N., Margaça, F.M.A., Miranda Salvado, I.M. and Santos Sousa, J., SANS investigation of polymer chain conformation and pore size distribution in organic-inorganic hybrid gels, Research Proposal to Lab. Léon-Brillouin, LLB, 1999. This proposal has received the highest classification (A) at LLB Tables Rondes 1999.

Further work

First and foremost for the swift progress of the planned activities of the hybrids project the commissioning of EPA.is required. Irradiation of x=0 samples using the 60Co Gamma Irradiation Unit, UTR, will be performed to promote radiation induced cross-linking that will also be used as a further variable to act on sample properties. It is expected that cross-linking in the organics increases the temperature stability of the hybrid material. Then, work will be extended to $x \neq 0$ samples, as the kinetics of gel formation change significantly with the content of the second component and so do the properties of the inorganic matrix when compared with pure silica.

* Funding: Contract PRAXIS/C/CTM/12212/1998, 14×10^6 PTE for two years, **ITN** and UA, and neutron beam time utilisation via EU 5th R&D, Framework Programme "Human Potential-Access to Research Infrastructures".
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Inorganic silica based materials

F.M.A. Margaça, J.S. Sousa[1], I.M.M. Salvado[2], J.Teixeira[3] and M. Misheva[4]

Objectives

Systematic investigation to correlate microstructure, macroscopic properties and processing conditions of inorganic silica based materials of the system (100-x)SiO_2.xMO_2 (M=Ti, Zr), prepared by the sol-gel process.

Results

In the course of a multi-annual project, samples of materials belonging to the above system were prepared by sol-gel, with high purity and homogeneity, at relatively low temperatures. The samples, prepared at Aveiro University, were investigated using both Small Angle Neutron Scattering, SANS, at Laboratoire Léon-Brillouin (CEA/CNRS, Saclay) and Positron Annihilation Spectroscopy, PAS, at Sofia University. Research was carried out on the influence of composition, pH [1] and heat-treatment on the nanostructure of silica, silica-titania and silica-zirconia gels. Results showed the variation of the properties of the final product with the processing conditions (e.g., Margaca *et al*., J. Non-Cryst. Solids, **209** (1997) 143; Miranda Salvado *et al*., J. Molec. Struct. **383** (1996) 271; Misheva *et al*., J. Phys. Cond. Matt. Supl. **8**, 34 (1996) 6313).

During 1999 SANS data from the study of the influence of the water/alkoxide molar ratio, R_w, on the structure of silica prepared by sol-gel with pH=9, shown below, were analysed and interpreted. Results showed that [1] a hierarchical microstructure, in which particles are packed in aggregates that are in turn packed, is found to be a reasonable model for these gels. Porosity exists at different length scales: large light scattering pores (>400 Å) between aggregates of particles; small angle scattering pores (<60 Å) between particles; and smaller (a few Å) pores within particles. The ratio R_w affects particle and aggregate sizes and thus porosity.

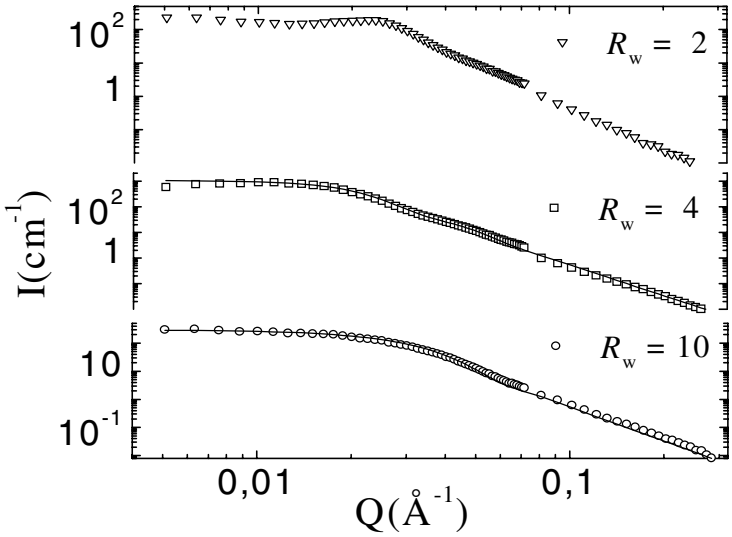

Fig. 1 – Experimental curves (scatter points) and associated fits (solid line) in individual log-log plots of I(Q) from 120ºC heat-treated samples prepared with R_W = 2, 4 and 10.

References

1. Margaça, F.M.A., Miranda Salvado, I.M and Teixeira J., Small angle neutron scattering study of silica gels: influence oh pH, J. Non-Cryst. Solids, 258 (1999) 70-77.
2. Miranda Salvado, I.M., Santos Sousa, J., Margaça, F.M.A. and Teixeira J., Structure of SiO_2 gels prepared with different water contents, Physica B, Proceedings of ENSC99, Budapest, Hungary, 1-4 September 1999, in press.

Further work

This project has been concluded. A natural extension of this work is now funded in the framework of Praxis XXI, to study the organically modified two-component inorganic oxide matrix with the addition of an organic constituent, to tailor the mechanical properties of the material.

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[3] Léon Brillouin Laboratory (CNRS/CEA), C.E. Saclay, 91191 Gif-sur-Yvette Cedex, France.
[4] Faculty of Physics, Sofia University, 5 J. Bourchier Boulevard, 1126 Sofia, Bulgaria.

Production and characterisation of colour centres in alumino-silicate crystals: topaz

C. Marques[1], A.N. Falcão, R.C. da Silva, E. Alves and L. Santos[2]

Objectives

Creating and characterising colour centres in natural colourless topaz by means of gamma-ray and neutron beam irradiation, and ion-beam implantation.

Results

A set of samples was prepared by irradiation with gamma-rays and neutron beams and annealed to produce stable blue colours in a reproducible way. RBS, RBS-C, X-ray diffraction, SEM and TEM, EPR as well as micro-Raman spectroscopy experiments were performed on colourless and coloured samples. The results obtained led to the conclusion that the ability to produce colour is very much correlated with the structure of the samples prior to irradiation.

Another set of samples was ion implanted. Co^+. Cr^+, Fe^+ and W^+ ion beams were used. Implantation doses and energies were respectively in the ranges 5×10^5 – 3×10^7 and 150 keV – 170 keV. After implantation, the surface of the crystals becomes amorphous. A high temperature annealing led to surface recrystallisation, which is accompanied by the loss of the Fluorine atoms. Samples implanted with Cr^+ and Fe^+ develop colour (green in the case of Cobalt and yellow in the case of Iron) whereas those implanted with Co^+ and W^+ do not.

Some of the results obtained were published in two papers [1,2], an University Degree thesis [3] was produced, and important guidelines for future work were established.

Fig. 1 – Natural colourless topaz (top left) and irradiation coloured topaz.

References

1. Marques, C., Falcão, A. N., da Silva, R. C., Alves, E., Annealing behaviour of natural topaz implanted with W and Cr Ions, *Nuc. Instr. and Meth. B*, in press.
2. Marques, C., Santos, L., Falcão, A. N., da Silva, R. C., Alves, E., Luminescence studies in colour centres produced in natural topaz, *J. Luminescence*, in press.
3. Marques, C., Characterisation of colour centres produced in natural topaz by irradiation with gamma-rays, neutron beams, and ion beam implantation, Graduation thesis (November, 1999).

Further work

Gamma-ray and neutron beam irradiated coloured topaz will be further investigated to determine which structural details are responsible for the correlation structure – color. Ion-implantation work will continue choosing different implantation conditions (temperature, energy) to avoid destruction of the surface structure. New ions will also be implanted. The re-crystallisation process of the damaged surface observed in the previously studied samples will be investigated as well as the role played by the implanted ions on the final color. The experimental work will be complemented with a theoretical calculation of the electronic structure as a function of unit cell content, looking for band structure, density of states, total energy and equilibrium geometries.

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Study of high temperature coated superalloys upon thermo-mechanical fatigue *

A. D. Sequeira, N. Franco[1], J. Bressers[2] and S. Peteves[2]

Objectives

The aim of the present project is to optimise the high-temperature properties of thermal barrier coatings and CoNiCrAlY coated SRR-99 single crystal superalloys under simulated service conditions using thermo-mechanical fatigue (TMF) test conditions.

Results

MCrAlY coatings are being increasingly used to protect high temperature structural superalloy components, both as buffer layers in thermal barrier coatings and as external protective layers, in high temperature applications. The good oxidation resistance of the coatings, makes them particularly interesting to protect turbine blades in jet engines, since it allows an increase of working temperature of the engines which leads to an increase of efficiency and reduction in fuel consumption.

The working conditions at various regions of a turbine blade were simulated by different thermo-mechanical fatigue (TMF) cycles. Life tests performed at high strain ranges (0.65% - 1.0%) and interrupted tests at low strain ranges up to 0.5% both in-phase and out-of-phase conditions.

The residual stress measurements were performed in the surface of the coating at room temperature after each test to study their evolution as the TMF test progresses [1]. The residual stress data was analysed using the *Sin^2 method* in a biaxial approximation.

References

1. Sequeira, A.D., Moretto, P. and Bressers, J.. Residual Stress and Microstructure of CoNiCrAlY coated SRR-99 upon Thermo-mechanical Fatigue. *Materials Science Forum* **Vol. 323** (1999) 748.

Further work

The study of this system will proceed with the high temperature measurements using the Hotbird. The in-situ experiments will allow to expand considerably the knowledge of the residual stress state and decomposition of this system.

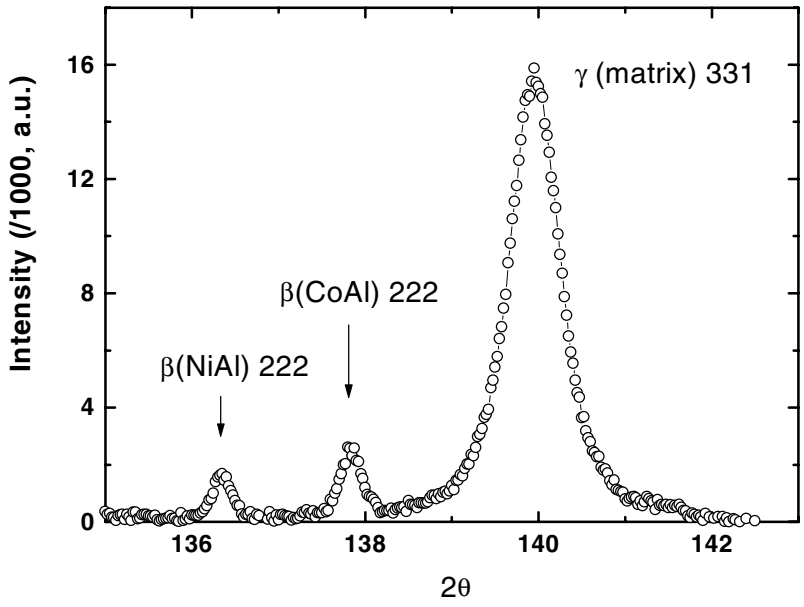

Fig. 1 – X-ray diffraction pattern of the CoNiCrAlY coating showing the peaks corresponding to the three main phases present at the surface after an out-of-phase TMF test, $\Delta\varepsilon$=0.7, R=-∞, 5065 cycles.

* Funding: Contract PRAXIS PCEX/P/FIS/21/96 (40 ×10^6 PTE).

[1] ITN MSc student.
[2] Institute for Advanced Materials, PO BOX 2, 1755 ZG Petten, The Netherlands.

Reconstruction of high temperature single crystalline aeronautical components through the deposition of overlay coatings and TBCs by laser cladding

P. Ferreira[1], R. Vilar[1] and A.D. Sequeira and R. C. da Silva

Objectives

The initial aim of the study was the use of laser cladding to produce polycrystalline coatings on single crystalline superalloys with low porosity and high oxidation resistance at high temperature. It is very importance to produce coatings free of defects (pores, inclusions) since these defects are associated with crack initiation and accelerate thermal degradation of the coating and subsequently the substrate.

Results

Coatings were deposited initially on polycrystalline superalloy samples and at a later stage in single crystalline substrates. The coatings have been characterised by microscopic techniques as well as X-ray diffraction, Rutherford backscattering and Channelling. To our surprise we have managed to go beyond that initial idea and produced single crystalline coatings that are coherent with the substrate with only a small mismatch. This process is not yet being used in industry and is crucial to allow to repair the very expensive single crystalline turbine blades.

Additionally, this technique proved to be an interesting alternative to the conventional deposition techniques (spraying) since it allows, in a single operation, to produce coatings with thickness from 50 to 1000 □m, free from pores and inclusions and excellent adhesion. This may prove to be competitive with the current commercial materials. The laser process is also an alternative to the conventional furnace thermal treatments used to improve adhesion of the coating. In fact, the high cooling speeds observed in these processes produce very fine microstructures, supersaturated solid solutions and metastable compounds, with exceptional functional characteristics. Since the energy density used is several orders of magnitude higher then the ones used in conventional methods, the time of interaction is very short and the energy transfer to the substrate reduced.

Further work

We intend to improve the deposition process and extend it to more complex shaped samples. Contacts have been initiated with a company that repairs turbine blades to use the process in industry.

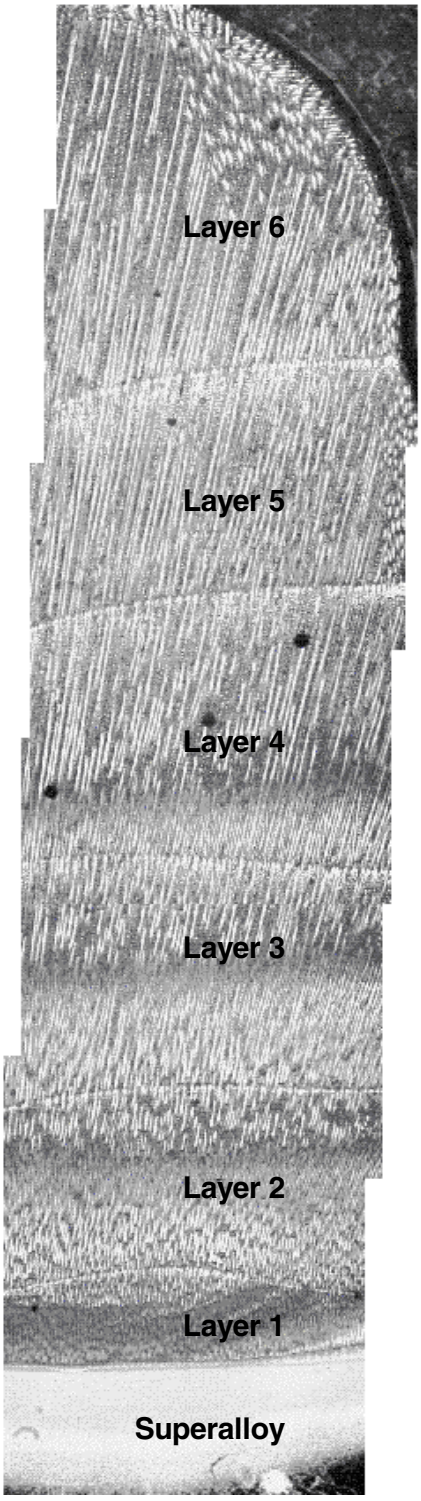

Fig. 1 – The microstructure of the single crystalline multilayer NiCrAlY coating. 6 layers have been deposited on top of the superalloy. The brighter regions are dendrites.

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Design optimisation of X-ray diffractometers - Generalization of the classic formalism for any type of source

N.R. Pinhão and A.D. Sequeira

Objectives

The aim of this project is the design optimisation of diffractometers. This consists in finding the diffractometer geometry that leads to the highest detector count-rate for any given value of the resolution. To study decomposition processes it is necessary to determine lattice parameters of coherent phases at different stages of the thermal cycle. Thus, a high angular resolution to resolve Bragg peaks at nearby positions is needed. However, to determine residual stresses medium resolution suffices. In the latter case the most adequate beam shape is point like, whereas for the high-resolution measurements a line shaped beam is better suited.

In some experiments, e.g. high-angle reflections at high temperature, even when an intense X-ray source is used, the diffracted beam is very weak making it quite difficult to orient single crystals at high temperature. Such measurements demand an optimised diffractometer design.

Results

The mathematical expressions of the Bragg peak intensity and its full width half maximum were considered in terms of the angular divergences of the incident and diffracted beams and of the mosaicity of both the monochromator and the sample. The general results were then applied taking into account the actual diffractometer components. Namely, the use of a position sensitive detector and different monochromator crystals were considered.

After the presentation of these results [1] in international event it was verified that the large companies (Philips, Bruker AXS, and all the other maker) that produce and sell X-ray diffractometers still use erroneous formalism in their software packages to determine intensities and experimental resolutions. The reason is that they use the formalism developed in the late fifties and early sixties that was developed for neutrons but the X-ray diffractometers use monochromatic radiation! (Caglioti G., and Ricci, F.P. *Nucl. Instr. and Meth*. **15** (1962) p.155)

References

1. Margaça, F.M., Pinhão, N.R. and Sequeira, A.D.. Design Optimisation of a High-temperature X-ray Diffractometer for in-situ Residual Stress Analysis and Lattice Mismatch Determination. *Materials Science Forum* Vol. **322** (1999) 168.

Further work

Currently a generalisation of the treatment and its application to specific diffractometer geometries is under way.

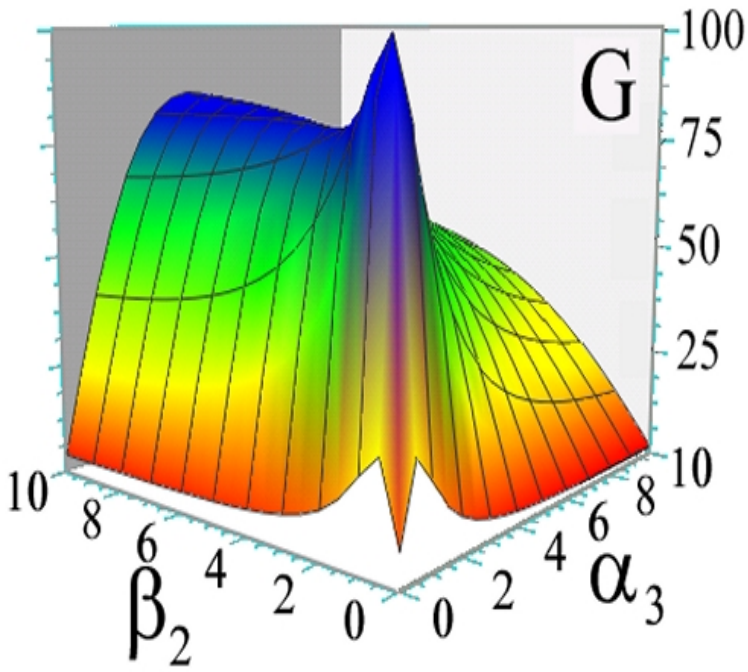

Fig. 1 – The dependence of the *optimisation function* G on the mosaicity of the sample and the divergence of the beam between the sample and detector.

X-Ray and Neutron Beam Instrument Optimisation

F.M.A. Margaça, A.N. Falcão, A.D.Sequeira, J.F. Salgado and F.G. Carvalho

Objectives

Optimisation studies of neutron beam instruments were originally motivated by the wish to make neutron scattering techniques available locally to interested users by implementing as performant as possible neutron scattering facilities at the Portuguese Research Reactor, RPI. Due to the modest thermal neutron flux available (2×10^{13} $s^{-1}cm^{-2}$) and the absence of a cold source, instrument design optimisation and improved beam-tailoring adapted to the reactor parameters is particularly important in the case of RPI to achieve good instrument performance. Results so far published have been acknowledged to be of a wider interest.

Results

The purpose of instrument design optimisation is to find the design associated with the highest possible detector count rate for a given resolution or, conversely, the best possible resolution for a given count rate. A few such studies carried out by the Group of Condensed Matter Physics are referred below. Particularly important are those that were applied to the EPA spectrometer, using optimisation criteria applicable to SANS instruments subject to the specific constraints of space and geometry of the RPI facility and of the neutron area detector (Margaça *et al*., *Nucl. Instr. Meth.*, ***A* 274**, (1989) 606; *J. Appl. Cryst.* **24** (1991) 994 and Falcão *et al*., *J. Appl. Cryst.* **27** (1994) 330). Optical effects on neutron guide tubes were also studied, using computer simulation (Falcão and Mortensen, Riso-R-566 (1989) 52) and analytical methods (Margaça et al. *J. Appl. Cryst.* **24** (1991) 531) and the optimised geometry for a stress neutron diffractometer was discussed (Margaça, in NATO ASI Series E: Applied Sciences Vol 216 (1992) 301).

The experience gained in the latter study has recently been applied to the design of an X-ray diffractometer for stress measurements and lattice mismatch determinations [1]. As part of the EPA project, the efficiency of the direct in-pile EPA neutron source (a disk-shaped light water volume at room temperature) was studied by Monte-Carlo simulation [2]. In another development the implementation of the concept of converging multichannel collimation to enhance the performance of a SANS instrument through improved use of the neutron source available is under investigation. First results indicate that important detector count rate gains for constant instrument resolution may be obtained [3].

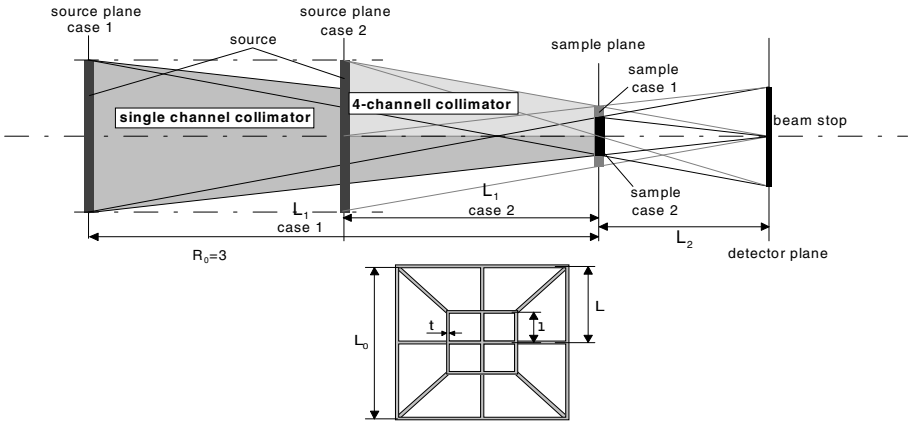

Fig.1 – Schematic representation of a matched SANS layout, equipped with one converging channel or with four converging channels.

References

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2. Falcão, A.N., Gonçalves, I.F. and Salgado, J.F., Efficiency of a thermal neutron scatterer with the shape of a flat disk studied by Monte-Carlo simulation, Proceedings of Vth Workshop on Nuclear Physics of the 2nd Int. Symp. on Nuclear and Related Techniques in Agriculture, Industry and Environment, NURT99, Havana, Cuba, 26-29 October, 1999.
3. Margaça, F.M.A., Salgado, J.F. Falcão A.N., Carvalho, F.G. "Multiple-Channel Collimation for improved Performance of SANS Instruments", Physica B, Proceedings of ENSC99, Budapest, Sept.1999, in press.

Further work

The concept of a 2D-converging multichannel collimator with adjustable geometry is presently under elaboration. A project proposal concerning this subject is being submitted to the National Foundation for Science&Technology for financial support from SAPIENS 99. In 1999 the Group participated in putting together a proposal for a research and technological development project LAMDET (Large Area Multi-wire Detectors for Neutron Experiments) involving other five partners from France and Hungary. The project is submitted for financial support from the EC for shared-cost RTD actions.

Development of a remote control and data analysis software for the Hotbird

N. Franco[1], J. Neves and A.D. Sequeira

Objectives

The aim of the current study is to develop software for remote control of hardware, data acquisition and data analysis for the X-ray diffractometer Hotbird. This involves the development of software in LabView and also of electronic components for interfacing with the hardware.

Results

The remote control system for the Hotbird was developed and it includes six main aspects: 1) Control of the sample goniometer, i.e. four rotation axis (θ, ψ, φ and 2θ) and three linear stages (x,y,z) and the monochromator's goniometer; 2) setting and monitoring experimental parameters (e.g. sample temperature, vacuum); 3) perform the data acquisition from the position sensitive detector; 4) control of the x-ray generator; 5) data analysis; and 6) account for the safety operational conditions (e.g. the temperature of the beryllium window, pressure in the vacuum chamber or violation of the radiation field). All this activities and monitoring are performed, continuously and simultaneously, by a redundant system of two computers protected by a UPS.

This software package was implemented using the graphical programming language *LabView* which also executes external code in other languages (e.g. C code) to access specific hardware. The two computers run in parallel some common routines and also specific applications that perform continuously bilaterally checks.

As a result of this work a paper was submitted to an international conference to be published in the journal *Materials Science Forum*.

Further work

Currently, additional experimental procedures are being developed, namely for the determination of textures and the alignment of single crystals.

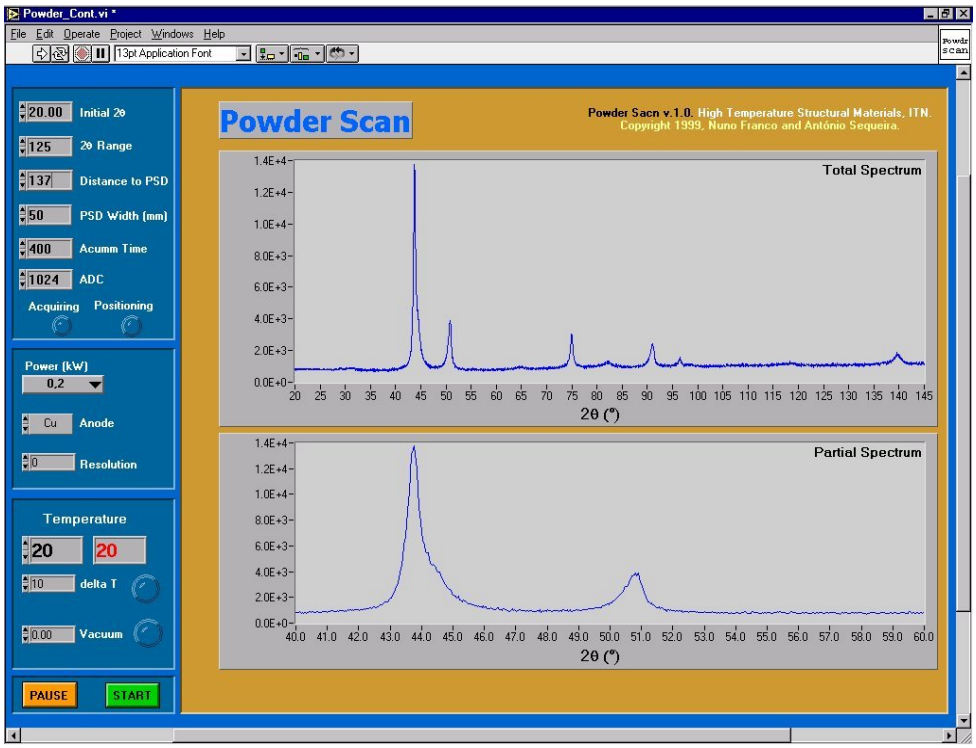

Fig. 1 – The experimental procedure Powder Scan.

[1] ITN MSc student.