Condensed Matter Physics

Introduction

Results of current research and progress in the development of experimental facilities is reported.

Current research covers a range of material systems whose study requires the utilisation of a variety of tools among which radiation probes – mainly low energy neutrons and X-rays but also electrons and visible light – occupy a prominent place. For historical and for objective reasons neutron scattering has a special place which is not unrelated to the perception of its importance for improving the utilisation of the local research reactor and developing a user community in the country. It is, in fact, considered a strategic aim to construct 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 exchange with foreign scientists and institutions.

In this context, two new neutron instruments are expected to become operational during 1999: 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 "banana" multidetector and a focusing crystal monochromator.

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.

The construction of a new laboratory centered on the Hotbird, a *high resolution X-ray diffractometer*, is reaching its final stages. This instrument will be soon carrying out diffraction experiments *in situ* at high temperature. Experiments at high temperature, in particular on single crystalline samples, are very useful and also very rare. The Hotbird is intended to study high temperature phenomena in *superalloys*, ceramics and semiconductors, and residual stresses.The instrument will be particularly suited to perform determination of internal strains, lattice mismatches between coherent phases, residual stresses and to observe the *in-situ* formation of intermetallic precipitates in implanted metals and semiconductors.

Commissioning such a diffractometer at ITN will enable carrying out locally highly specialized experiments that will impart substance to collaborations with foreign teams and the training of young scientists.

Several joint research projects are currently under way in partnership with groups in and outside the country. 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). A new project in Biomedicine is in preparation involving a Biomedical Institute in Coimbra that aims at developing a new polyurethane based surgical adhesive.

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).

Research Team

Researchers –	5	(5 PhD)
Research Students –	2 *	
Undergraduate Students –	4	
Technicians –	-	

* FTE (full time equivalent)

Publications

Journals –	1 in press
Proceedings –	3
Special Publ. –	3
Progress Reports	1
Conf. Commun.:	9
Theses:	
Lic. –	2

10^3 PTE

Expenditure:	**128 765**
Missions:	1 255
Other Expenses:	17 743
Hardware & Software:	262
Other Equipment:	109 505

10^3 PTE

Funding:		**121 599**
OE/ITN	OF	44 892
	PIDDAC	59 295
External Projects:	1997	12 563 (1)
	1998	4 850

(1) Funding not used in 1997

SILICA BASED VITREOUS MATERIALS

Positron Annihilation Spectroscopy Applied on Sol-Gel Prepared SiO_2

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Abstract
Positron Annihilation Lifetime and Doppler Broadening of annihilation line techniques have been used to obtain information about the small-pore structure of SiO_2, prepared by the alkoxide method in different experimental conditions. Samples, prepared in strong acidic environment (pH=2) contain only small pores with mean radius R~3 Å, while those prepared at pH=6 and pH=9 contain pores of two sizes, R~3 Å and R~14 Å. The influence of pH, water/alkoxide molar ratio and temperature of heat-treatment of the samples on their pore structure has been studied.

Journal of Phys. C: Condens. Matter (in press).

SANS Study of Silica Gels: Influence of pH

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[2]*Glass and Ceramics Engineering Dept., UIMC, Aveiro Univ., 3810 Aveiro, Portugal*
[3]*Léon Brillouin Lab. (CNRS/CEA), C.E. Saclay, 91191 Gif-sur-Yvette Cedex, France*

Abstract
The technique of Small Angle Neutron Scattering, SANS, has been used to investigate the microstructure, at nanoscale, of SiO_2 gels at different processing stages. The samples were prepared by the alkoxide route of the sol-gel process with different pH values. They were measured as xerogels after heat treatment at different temperatures and as wet gels at gel point and after ageing at 60º C. SANS measurements confirmed that pH has a strong influence upon the nanostructure of gels. The present work reports the main SANS results obtained in this investigation and their interpretation.

Journal of Non-Cryst. Solids, submitted.

Current Work

Research on Silica Based Materials

F.M.A. Margaça[1], I.M.Miranda Salvado[2], J.Teixeira[3] and M. Misheva[4]
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The study of inorganic gels of the system (100-x)SiO_2.xMO_2 (M=Ti, Zr), with x ≤ 10% mol was pursued. Samples are prepared and characterised at Aveiro University by I. Miranda Salvado. The nanostructure of the samples is investigated using small angle neutron scattering (SANS) by F. Margaça, in collaboration with J. Teixeira of Laboratoire Léon-Brillouin while positron annihilation **s**pectroscopy (PAS) measurements are carried out at Sofia University, through a collaboration with M. Misheva's group. Results have been reported in several papers published in international scientific journals.

In the year 1998 the study of the dependence of gel properties on processing conditions was concluded for the inorganic gels of the system referred above. An application for support by the Praxis XXI Programme was prepared and submitted to study the organically modified two-component inorganic oxide matrix. We propose to prepare and characterise materials with an inorganic constituent composition of (100-x)SiO_2.xMO_2 (M=Ti, Zr) covalently linked with an organic component of polymeric material such as PDMS. The purpose of the project is to carry out a systematic investigation of the hybrids so obtained in order to find out the dominant relationships between microstructure (mainly at the nanoscale), macroscopic and other properties and processing conditions. We will focus on the influence of parameter x, polymer concentration and molecular weight and processing conditions. This project is a natural extension of the research carried out in the near past but represents a broadening of the research effort related to novel applications of inorganic gels. The addition of an organic constituent aims at tailoring the mechanical properties of the end material, since different polymer concentrations and different polymer molecular weights lead to materials with different properties ranging from those characteristic of conventional glasses to those typical of elastomers.

HIGH TEMPERATURE STRUCTURAL MATERIALS

The Evolution of the Microstructure and Crack Propagation of CoNiCrAlY Coated Superalloys Upon Thermo-Mechanical Fatigue

A.D. Sequeira[1] and J. Bressers[2]
[1]Physics Dept., Nuclear and Technological Institute, Estrada Nacional 10, 2685 Sacavém, Portugal
[2] Institute for Advanced Materials, PO BOX 2, 1755 ZG Petten, The Netherlands.

Abstract

As a consequence of the optimisation of *creep strength* of superalloys the concentration of oxidation-resistance elements like Cr have been reduced. Thus, the most modern superalloys are mechanically stronger yet more vulnerable to oxidation and corrosion and need a protective layer to cope with the highly corrosive atmospheres found in certain service conditions, e.g. in jet engines and power plants both in marine or land environments.
In the present study the material consists of a SRR-99 single crystalline substrate with a protective overlay coating of CoNiCrAlY. These coatings have a very good oxidation resistance and a good ductility in particular at high temperature. However, under thermo-mechanical fatigue (TMF) they have a detrimental effect on the behaviour of the substrate. One needs to understand the reasons for this behaviour to aim for the improvement of their properties and ultimately for the development of life prediction methodologies.
In this study the working conditions at various regions of a turbine blade were simulated by different TMF cycles. Life tests performed at high strain ranges (0.65% - 1.0%) and interrupted tests at low strain ranges up to 0.5%.
For the characterisation of the system a set of complementary techniques was used. The *microstructure* of both coating and sub-coating regions are studied by transmission and scanning electron microscopy, the phase identification was performed using X-ray diffraction and at a microscopic scale using CBED, the study the *residual stresses* in the main phases was carried out by XRD.

The TMF behaviour of the material and the crack propagation under the different TMF test conditions is presented and the two main mechanisms for the relieve of the residual stresses are identified and described.
From this study can be concluded that under small strain ranges most of the damage accumulates in the coating. However, depending on the TMF test conditions the crack initiation and crack propagation differs considerably. Whereas in the out-of-phase tests the material fails owing to defects originated in the coating, in the in-phase tests the material fails at the substrate.
It is expected that from the identification of the micromechanisms leading to failure will give new insights for the development of modelling procedures for life prediction of coated superalloys.

Proceedings of ***EuroMat98,*** Lisbon, Portugal (1998) 121-130.

The Use of Transmission and Scanning Electron Microscopy to study Thermomechanically Fatigued CoNiCrAlY Coated Superalloys

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Abstract
This study is aimed to support the efforts for developing life prediction methodologies of coated superalloys under *thermo-mechanical fatigue* (TMF). To describe the behaviour of these materials one needs a deep understanding of the mechanisms of damage that occur at the service temperature and lead to failure. Therefore, a thorough experimental characterisation of coated superalloy systems is necessary. The present paper illustrates some microstructural changes and the crack propagation observed in CoNiCrAlY coated SRR99 superalloy under different thermo-mechanical fatigue test conditions. The complex microstructure of the interface region is described and the main mechanisms for residual stress relieve will be identified [1] and discussed at FÍSICA '98.

The coating. Overlay coatings, as CoNiCrAlY, are being increasingly used to protect structural superalloy components, both as buffer layers in thermal barrier coatings and as external protective layers, in high temperature applications, owing to their very good oxidation resistance and good ductility in particular at high temperature. An advantage of overlay coatings when compared to diffusion coatings is that they allow to tune their composition to adapt to the type of application.

However, the different thermal and mechanical properties of the two materials, coating and substrate, when subjected to changes of temperature and mechanical strain produce large residual stresses at their interface. These internal stresses induce several mechanisms of damage, e.g. creep and cracking, that tend to reduce the useful life of the component. In order to understand this behaviour one needs to identify the mechanisms of damage that are active under service conditions.

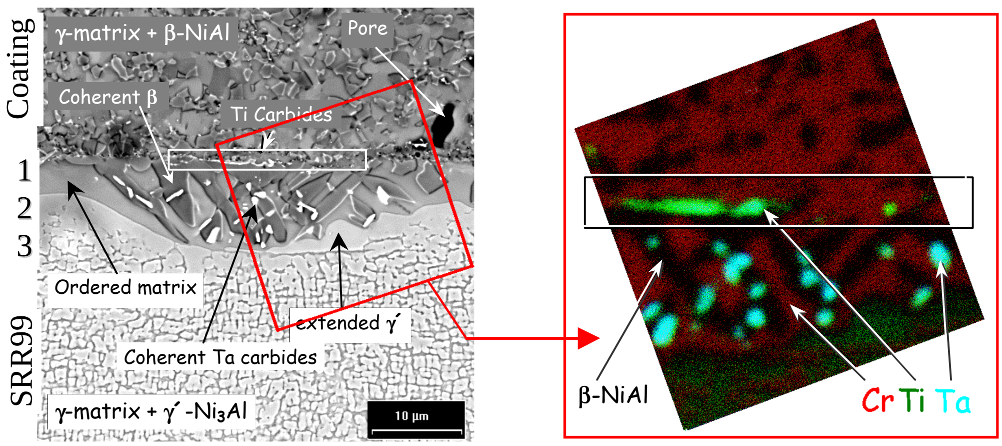

Fig. 1 – Back scattered electron image of the interface region of the as-received material (left) and false colour EDX mapping (right) for Cr, Ti and Ta. The dark regions are coherent β-NiAl precipitates.

The working conditions at various regions of a turbine blade were simulated by different thermo-mechanical fatigue (TMF) cycles as described in [2]. A set of complementary techniques was used for the characterisation of the system. The microstructure of both coating and sub-coating regions are studied using transmission and scanning electron microscopy,

phase identification was performed using X-ray diffraction and, at a microscopic scale, using CBED have been reported elsewhere. The evolution of the *residual stresses* during TMF testing was carried out by XRD and is reported in [2]. Additional details can be found in [3].
The *interface region*, or *diffusion region*, stands between the single crystalline substrate, SRR-99 superalloy and the CoNiCrAlY polycrystalline coating. It is very narrow when compared with other types of coating (e.g. diffusion coatings) and it represents only a few percent of the coating thickness. However, it is the most complex region with a large variety of phases. One may distinguish three different regions at the interface (see Fig. 1). A polycrystalline region on the coating side (region-1) and two single crystalline regions: an intermediate region-2 (the real interface region) and one on the substrate side (region-3). The two extreme regions are very narrow and connect continuously to the coating and substrate respectively. Region-1 shares the same γ-β structure of the coating and is readily identifiable by the high concentration of titanium carbides that align themselves in a row along the interface where small pores can also be found. Region-3 is an ordered $L1_2$ single crystalline structure and consists in a continuous

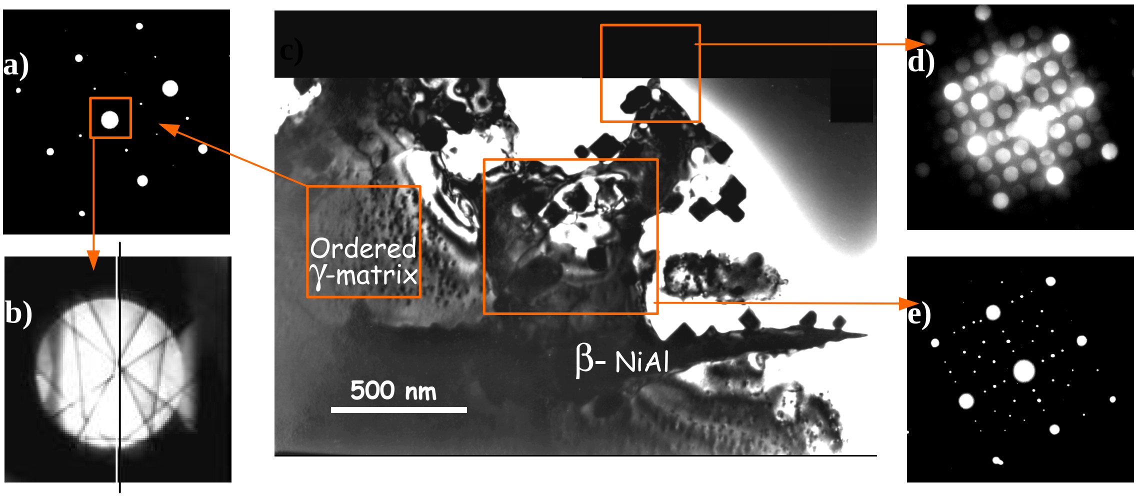

Fig. 2 - TEM bright-field image (c) showing a detail of the interface region-2. Selected area diffraction patterns (a,e) and CBED patterns (b,d) were used to identify the main phases present. The matrix was found to be ordered with a tetragonal distortion (b).

domain of γ'-phase. The intermediate region-2 is the most complex of the three as shown in the TEM image of Fig. 2c. The matrix consists of an ordered f.c.c. (Fig. 2a) with a local tetragonal structure illustrated by the loss of the mirror symmetry in the high-order Laue-zone lines pattern depicted in Fig. 2b. The dark cuboidal precipitates are coherent Ta carbides (M_6X) showing a cube-cube orientation with the matrix (Fig. 2d). The elongated dark precipitates consist of β-NiAl with a B2 structure.

References

[1] A.D. Sequeira and J. Bressers, *The Evolution of the Microstructure and Crack Propagation on CoNiCrAlY Coated Superalloys upon Thermo-mechanical Fatigue*. *EuroMat98* (1998).

[2] Communication by S. Rebelo *et al*. in these proceedings.

[3] A.D. Sequeira and J. Bressers, *The Evolution of the Residual Stresses of CoNiCrAlY Coated Superalloys upon Thermo-mechanical Fatigue*. ***Materials Science Forum*** (1998).

Communication to: *11th National Conference of Physics*, Portuguese Physical Society (1998) 509-510.

The Use of $sin^2 Y$ *method* for the Determination of Residual Stresses on Thermomechanically Fatigued CoNiCrAlY Coated Superalloys

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Abstract
As a consequence of the *creep strength* optimisation of superalloys, the concentration of oxidation-resistance elements like Cr have been reduced. Nowadays, superalloys are mechanically stronger yet more vulnerable to oxidation and corrosion and need a protective layer to cope with the highly corrosive atmospheres found in certain service conditions, e.g. in jet engines and power plants both in marine or land environments. This becomes increasingly important as the operating temperature increases in order to improve efficiency.

Overlay coatings, as CoNiCrAlY, are being increasingly used to protect structural superalloy components, both as buffer layers in thermal barrier coatings and as external protective layers, in high temperature applications, owing to their very good oxidation resistance and good ductility in particular at high temperature. An advantage of overlay coatings when compared to diffusion coatings is that they allow to tune their composition to adapt to the type of application.

However, the different thermal and mechanical properties of the two materials, coating and substrate, when subjected to changes of temperature and mechanical strain produce large residual stresses at their interface. These internal stresses induce several mechanisms of damage, e.g. creep and cracking, that tend to reduce the useful life of the component [1]. In order to understand this behaviour one needs to identify the mechanisms of damage that are active under service conditions.

The aim of the present paper is to present and discuss residual stress measurements performed at the surface of CoNiCrAlY coated SRR-99 single crystal superalloys upon TMF.

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 (see Fig.1).

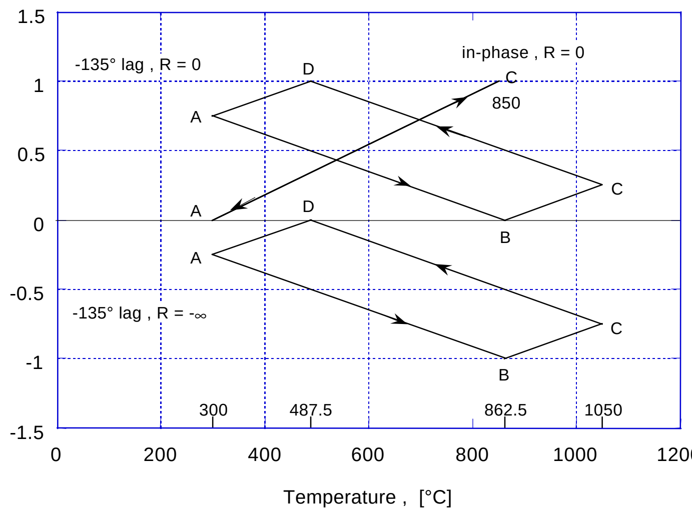

Fig. 1 - The three TMF cycles used. In-phase with R=0, out-of-phase R=0 and out-of-phase R=-∞.

A set of complementary techniques was used for the characterisation of the system. The microstructure of both coating and sub-coating regions are studied using transmission and scanning electron microscopy, phase identification was performed using X-ray diffraction and, at a microscopic scale, using CBED are reported in the paper by *A.D. Sequeira et al.* in these proceedings and in [2]. The evolution of the *residual stresses* during TMF testing was carried out by XRD and will be reported here. More details can be found in [3].

The residual stress data was collected at the Philips diffractometer. Data analysis was performed method using the *"Sin^2 Y method"* in a biaxial approximation.

The figure shows the dependence of the residual stress as a function of the strain range $\Delta\varepsilon$. Only the residual stress measurements for the matrix γ and in the direction parallel to the stress are shown. The results are plotted as a function of the strain range and the cycle number.

The highly compressive residual stress of the as-received material has been proved to be an artefact produced by the machining of the test piece which produces a highly disturbed surface and induces intense residual stresses. After annealing the sample at 870^{o}C for a few hours the sample surface relaxed and show the expected residual tensile stress, $\sigma(\gamma)$ = + 243 MPa. A detailed interpretation of the residual stress results will be given in the communication.

References

[1] J. Bressers, K. Ostolaza and M. Arana, *Coating induced life reductions of single crystal superalloy gas turbine blade materials*, in Elevated Temperature Coatings: Science and Technology II, N.B. Dahotre and J.M. Hampikian eds., ***The Minerals, Metals and Materials Society***, 1996, 275-285.

[2] A.D. Sequeira and J. Bressers, *The Evolution of the Microstructure and Crack Propagation on CoNiCrAlY Coated Superalloys upon Thermo-mechanical Fatigue*. ***EuroMat98*** (1998).

[3] A.D. Sequeira and J. Bressers, *The Evolution of the Residual Stresses of CoNiCrAlY Coated Superalloys upon Thermo-mechanical Fatigue.* ***Materials Science Forum*** (1998).

Communication to: *11th National Conference of Physics*, Portuguese Physical Society (1998) 515-516.

Simulation Electron Microscopy Images And Its Use For The Characterisation Of Materials

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Introduction

Transmission electron microscopy (TEM) images, namely high-resolution (HREM), can not be interpreted directly as atom images or columns of atoms. These images depend on the distribution of potential in the interior of the crystal and on the optical systems used. The latter are characterised by a well known transfer function, that modifies the amplitude and phase of the Fourier transform components of the observed function. The knowledge of the intervening factors in the formation of these images allow their reliable simulation and physical interpretation.

The current communication describes generically the capabilities of the EMS software package [1] recently installed at ITN. An example will be given to illustrate its potentiality for the simulation of convergent-beam electron Diffraction (CBED) images.

The EMS [1] is composed of many small programs meant to be used in batch mode. They are divided in five different groups:

- ***Crystallography Programs*** *- Determination of Bravais lattices and diffraction patterns; visualisation of crystalline structures; determination of High order Laue zones (HOLZ) patterns (kinematic approximation); stereoghrams; etc…*
- ***Bloch wave calculations*** *- determination of convergent beam electron diffraction patterns (CBED); wave functions; etc…*
- ***Multislice Calculations*** *- calculation of diffraction patterns; Fresnel propagtors and transmission functions;*
- ***Calculation of images*** *- determination of HREM, CBED, HOLZ images, hologhrams; etc.*
- ***Utilities*** *- E.g. for Manipulation of files.*

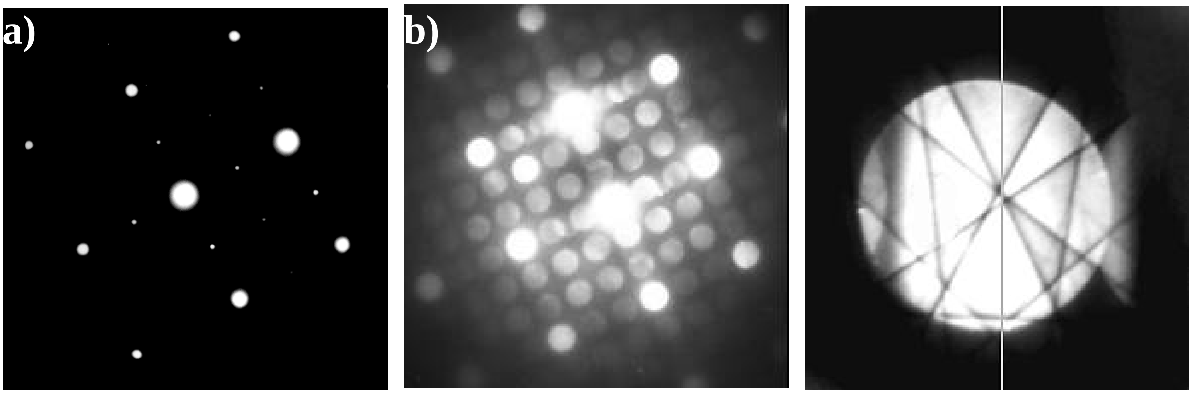

Fig. 1. - Diffraction patterns: (a) conventional DP (b) CBED and (c) HOLZ lines.

Example. Origin of the higher order Laue zone (HOLZ) lines. When the probed volume of the sample is flat and free of strain the diffraction maxima contain the so-called higher order Laue zone lines, see Fig. 2. They result from scattering at higher order zones and occur in pairs of bright and dark lines. To each bright HOLZ line existing in a particular high order zone reciprocal disk (Fig. 1b, lines not visible in Fig.2 field of view) a corresponding parallel dark HOLZ line appears in the transmitted zero order disk. These dark lines are also called defect lines and their position is highly sensitive to the lattice parameter of the probed region due to the high momentum transfer involved in the scattering. Variations of 10-4 in the lattice parameter produce noticeable changes in the relative position of the lines allowing the high-precision determination of lattice parameters.

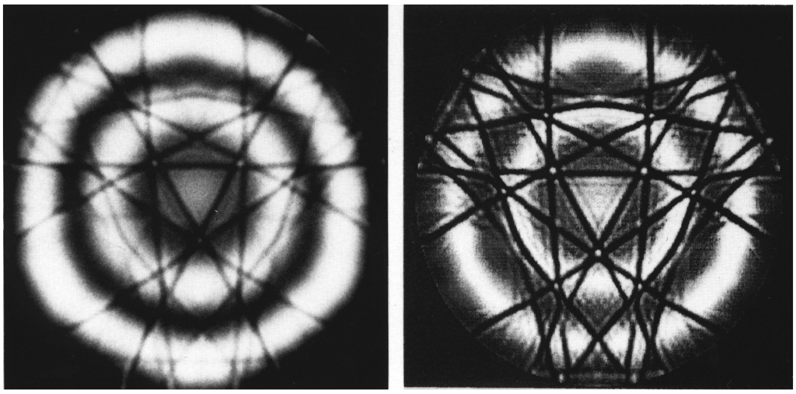

Fig. 2 – CBED patterns corresponding to the [111] pole of a Si crystal used as standard: (a) experimental; (b) simulation.

Determination of local lattice parameters on a superalloy. A Philips EM400 electron microscope was used to determine the lattice parameter of the phases present by convergent-beam electron diffraction (CBED). This technique allows the lattice parameter variations to be determined from the displacement of the higher-order Laue-zone (HOLZ) lines in the central disk of the diffraction pattern.

For the accurate determination of the lattice parameter values one needs to know the effective acceleration voltage of the microscope. In the present study a silicon crystal was used routinely before and after every TEM session. The [111] pole was used. The experimental CBED patterns were matched with the simulated ones using the accelerating voltage as fitting parameter. Fig. 2 shows an example of an experimental pattern (2a) and the corresponding simulation (2b).

The local character of this technique allows the determination of lattice constants even in narrow matrix regions between precipitates. The spot may be varied according to the characteristics of the region to be analysed. A relatively large (> 30 nm) spot may be used whenever a large strain free region was studied and reduced to smaller sizes (10 nm) in narrow matrix regions. To improve the visibility of the HOLZ lines and minimise beam contamination the patterns were recorded with a best possible vacuum. The determination of the lattice parameters is made by adjusting the experimental HOLZ line patterns with simulated ones. An example is depicted in Fig. 2. The fine dark lines inside the direct beam are the HOLZ lines. The thick dark “rings” in are related to the thickness of the sample. Each ring corresponds to a extinction length that is characteristic of the material and their number give the thickness of the sample in the region of observation.

The very low intensity of the HOLZ lines, in particular when using small probes, implies the use of extended exposures (up to a few minutes). Thus, unless the vacuum conditions are very good, contamination of the sample occurs and the pattern is lost before completing the measurement. In these conditions the quality of the image is degraded and some enhancements techniques are necessary to make quantitative determinations.

Although the values of the lattice parameters may only be determined by adjusting the experimental pattern with a corresponding simulation, some properties of the crystalline lattice can be determined directly by the visual observation of the CBED pattern. For instance, the properties that are related to symmetries of the HOLZ pattern can be accessed by a qualitative analysis.

References

[1] P.A. Stadelmann, ***Ultramicroscopy*** **21** (1988) 131.

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[3] A.D. Sequeira and Johan Bressers, *The Evolution of the Microstructure and Crack Propagation on CoNiCrAlY Coated Superalloys upon Thermo-mechanical Fatigue*. ***EuroMat98*** (1998).

Communication to: *11th National Physics Conference*, Portuguese Physical Society (1998) 511-512.

The Evolution of the Residual Stresses of CoNiCrAlY Coated Superalloys upon Thermo-mechanical Fatigue

A.D. Sequeira[1], P. Moretto[2] and J. Bressers[2]

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[2] *Institute for Advanced Materials, PO BOX 2, 1755 ZG Petten, The Netherlands.*

Abstract

Overlay coatings are being increasingly used to "protect" 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, in particular CoNiCrAlY 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.

However, the different thermal and mechanical properties of the two materials, coating and substrate, when subjected to large changes of temperature and mechanical strain produce large residual stresses at their interface. These internal stresses induce several mechanisms of damage, e.g. creep and cracking, that tend to reduce the useful life of the component.

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 aim of the present paper is to present and discuss residual stress measurements performed at the surface of CoNiCrAlY coated SRR-99 single crystal superalloys upon TMF.

The residual stress data was collected at the Philips diffractometer using the ω method. Data analysis was performed method using the "Sin^2 method" in a biaxial approximation. The figure shows the dependence of the residual stress as a function of the strain range $\Delta\varepsilon$. Only the residual stress measurements for the matrix γ and in the direction parallel to the stress are shown. The results are plotted as a function of the strain range and the cycle number.

The highly compressive residual stress of the as-received material has been proved to be an artefact produced by the machining of the test piece which produces a highly disturbed surface and induces intense residual stresses. After annealing the sample at 870°C for a few hours the sample surface relaxed and show the expected residual tensile stress, $\sigma(\gamma)$ = + 243 Mpa (see Figure). A detailed interpretation of the residual stress results is given.

Materials Science Forum, (in press).

Design Optimisation of a High-temperature X-ray Diffractometer for in-situ Residual Stress Analysis and Lattice Mismatch Determination

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Abstract
A multipurpose X-ray diffractometer, equipped with a high-temperature furnace, is being designed. It will be used to study in-situ decomposition phenomena in metallic alloys, to determine lattice parameters and residual stresses at high temperature.
Single crystalline samples are to be used in most of the studies. For that reason a high precision goniometer is required and is currently being built.
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. The design of such a multipurpose diffractometer has, therefore, to take into account that the layout of the instrument should be versatile to be set in different geometries with ease.
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.
The aim of the design optimisation study is to find the diffractometer geometry that leads to the highest detector count-rate for any given value of the resolution.
The mathematical expressions of the Bragg peak intensity and its full width half maximum are considered in terms of the angular divergences of the incident and diffracted beams and of the mosaicity of both the monochromator and the sample. Focusing effects are also discussed. The general results are then applied taking into account the actual diffractometer components. Namely, the use of a position sensitive detector and different monochromator crystals will be considered.

Materials Science Forum, (in press).

Current Work

Development of a CoNiCrAlY Overlay Coating by Laser Cladding and Characterisation using Electron Microscopy

***P. Ferreira*[1]*, R. Vilar*[1] *and A.D. Sequeira*[2]**
[1] *Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisboa Codex, Portugal*
[2] *Physics Dept., Nuclear and Technological Institute, Estrada Nacional 10, P-2685 Sacavém, Portugal*

Abstract
In order to increase the service temperature of single crystalline turbine blades one needs to improve their oxidation resistance. An effective way to protect high strength superalloys is to deposit a coating at their surface with good oxidation resistance. A common process used for the deposition is by plasma projection. However, these coatings show poor adhesion to the substrate and a high level of inclusions and pores. Thus, requiring subsequent thermal treatments to reduce porosity and increase adhesion.

The aim of this study is to produce coatings on single crystalline superalloys, with low porosity and high oxidation resistance at high temperature, by laser cladding. The importance of producing coatings free of defects (pores, inclusions) that are associated with crack initiation and accelerate thermal degradation of the coating and subsequently the substrate.

Laser cladding is an interesting alternative to these conventional techniques since it allows in a single operation to produce coatings with a thickness from 50 to 1000 μm, free from pores and inclusions and excellent adhesion. This may prove to 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. The characteristics of these processes are particularly adequate for the treatment of surfaces of materials with high specifications and high added value. 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.

The deposition process is being optimised in order to maximise the functionality of the coating-substrate system.

The coatings produced are being characterised in detail by microscopic techniques as well as X-ray diffraction techniques. These results will be compared with the ones from commercial coatings.

RADIATION INDUCED OPTICALLY ACTIVE DEFECTS

Current Work

Production and Characterisation of Colour Centres in Alumino-Silicate Crystals: Topaz

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Pure topaz is an alumino-silicate that is transparent throughout the visible region of the spectrum. It is well known that most topaz samples become coloured when bombarded with high-energy electrons, gamma-rays or neutron beams. It is also known that a controlled annealing of the defect structures produced upon irradiation can develop a stable blue colour in the samples. This process has been used to enhance the commercial value of the mineral.

Preliminary research work required for launching a project to produce and study colour centres in natural colourless topaz was performed. Samples originating from different extraction sites (in Portugal and abroad) were made available. Their chemical composition was determined by means of non-destructive techniques (RBS and PIXE). To improve crystalline quality, the samples followed an annealing protocol. The irradiation experiments were performed using fast neutron beams and ^{60}Co photon beams. Also, some samples were ion implanted with different doses of 170 keV Cr^+ or W^+ ions. Prior to and after irradiation the optical transmission of the samples was evaluated by spectrophotometry, and the crystalline quality checked by RBS-C. Subsequent annealing of the irradiated samples has proved successful in producing stable blue colours. It is possible to control the sample preparation procedure in such a way that reproducible stable colours can be obtained.

The samples were studied by RBS, RBS-C, X-ray diffraction, SEM and TEM, EPR and NMR, as well as micro-Raman spectroscopy. These studies were performed in collaboration with three departments of the Aveiro University: Chemistry Dept. (NMR); Ceramics and Glass Engineering Dept. (X-ray, SEM, TEM), Physics Dept. (EPR). The framework of a future collaboration with the Physics Department of Aveiro University was established.

INFRASTRUCTURE DEVELOPMENT

The Hotbird - a High-temperature X-ray Diffractometer for in-situ Studies – Remote Control and Optimisation

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Abstract
The *Hotbird* is a high-resolution multipurpose X-ray diffractometer equipped with a high-temperature furnace and a 4-circle goniometer to study both single and polycrystalline samples. This instrument is being designed and built at ITN(*). It will be used to perform high-temperature *in-situ* studies of decomposition phenomena in metallic alloys [1], to determine lattice parameters and residual stresses from room temperature up to 1400ºC [2]. The *Hotbird* will play an important role in activities of the group as a complement of the electron microscopy techniques currently in use [3].

Since the *Hotbird* is being projected and built from scratch it is necessary to develop all the necessary facilities for its functioning and control, which are assumed 'granted' in a commercial instrument. This demands a co-ordinated multidisciplinary teamwork.

This communication reports two, out of several, aspects addressed in the *Hotbird* project:

- The theoretical study of the design optimisation of the diffractometer. This is aimed to find the best compromise between intensity and resolution.
- The implementation of the remote control system of the *4-circle goniometer*, high-temperature control and data acquisition from the position sensitive detector.

Design optimisation. To study decomposition processes it is necessary to determine lattice parameters of coherent phases at different stages of the thermal cycle [2]. This requires a high angular resolution in order to resolve Bragg peaks at nearby positions is needed. However, to determine residual stresses medium resolution suffices [3]. 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. study of high-angle reflections at high temperature the diffracted beam is very weak making it quite difficult to orient single crystals at high temperature, even when an intense X-ray source is used. Such measurements demand an optimised diffractometer design.

Therefore, versatility must thus be taken into account on the design of such multipurpose diffractometer to allow the layout of the instrument to be set in different geometries with ease.

The aim of the design optimisation study is to find

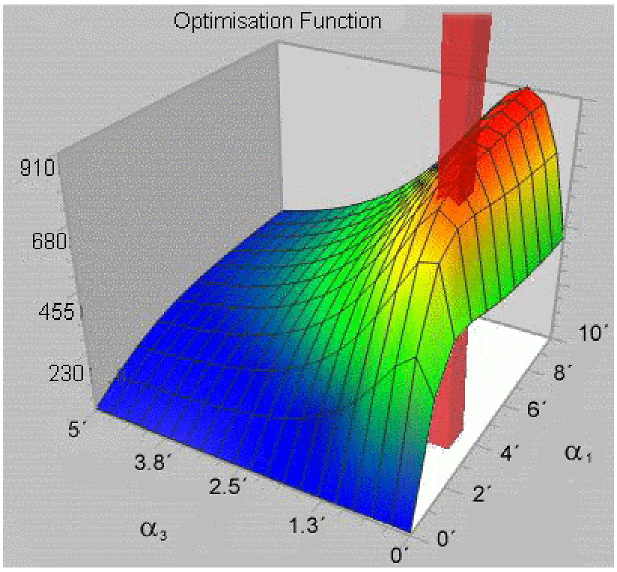

***Figure 1** - The dependence of the 'optimisation function' on two geometrical variables, the divergences a_1 and a_3.*

(*) See also the communication by A. Gomes *et al*. in these proceedings.

the diffractometer geometry that leads to the highest detector count-rate for any given value of the resolution.

The mathematical expressions for the Bragg peak *Intensity* and the *Full Width Half Maximum* (*FWHM*) [6] are considered in terms of the angular divergences of the incident and diffracted beams and of the mosaicity of the monochromator and the sample. Furthermore, an expression for an *'Optimisation Function'* is derived. This function has maxima when an optimised relationship between the relevant geometrical parameters is reached (an example for one specific case is shown in figure 1). Achromatic corrections as described in [7] and focusing effects are also addressed. The general results are applied taking into account the actual diffractometer components. Namely, the use of a position sensitive detector and different monochromator crystals are considered.

Remote control. **The aim of the current study is the development of an 'intelligent' remote control system for the Hotbird concerning the following requirements:**

- remote control of the 4-circle goniometer (four rotation axis θ,ψ,ϕ, 2θ and two linear stages X,Y), the monochromator's goniometer (θ,ψ,X,Y) and slits,
- setting and monitoring of experimental parameters (e.g. sample temperature, vacuum),
- data acquisition from the position sensitive detector,
- control of the X-ray generator,
- data analysis,
- account for the safety with respect to operational conditions (e.g. the temperature of the beryllium window, pressure in the vacuum chamber or violation of the radiation 'field').

All these activities have to be performed, continuously and simultaneously, by a redundant system of two computers protected by an UPS.

This software package is being implemented using the graphical programming language *LabView* that 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 bilaterally checks.

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[3] António D. Sequeira and Johan Bressers, *The Evolution of the Microstructure and Crack* ***Propagation on CoNiCrAlY Coated Superalloys upon Thermo-mechanical Fatigue.*** *EuroMat98.*

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[5] F.M.A. Margaça, M.M. van Overveld, N.R. Pinhão and A.D. Sequeira. *Design Optimisation of a High-temperature X-ray Diffractometer for in-situ Residual Stress Analysis and Lattice Mismatch Determination*. To appear in *Materials Science Forum* (1998)

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Communication to: *11th National Physics Conference*, Portuguese Physical Society (1998) 513-514.

Design and Construction of a High-temperature high-resolution X-ray Diffractometer for in-situ Studies - The 'Hotbird'

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Abstract

Hotbird is a *high-resolution X-ray diffractometer* equipped with a high-temperature furnace and a 4-circle goniometer to perform diffraction experiments *in-situ*, at high temperature, on both single- and polycrystalline samples. This instrument is being designed and built by the team at ITN(*). Such an instrument is rare and is not commercially available.

The *Hotbird* will be used for the characterization of high-temperature properties of structural materials, being particularly suited for the determination of residual stresses [1], lattice mismatches between coherent phases with high accuracy [2], to study *in-situ* formation of intermetallic precipitates in implanted metals and semiconductors from room temperature up to 1400ºC. This type of experiments have recently risen much interest in numerous research groups to study ceramics and *superalloys*(**).

This instrument will play an important role in activities of the group as a complement of the electron microscopy techniques currently in use [3]. The commissioning of such a diffractometer at ITN will enable the team to carry out, locally, highly specialized experiments that will impart substance to collaborations with national and foreign teams and the training of young scientists.

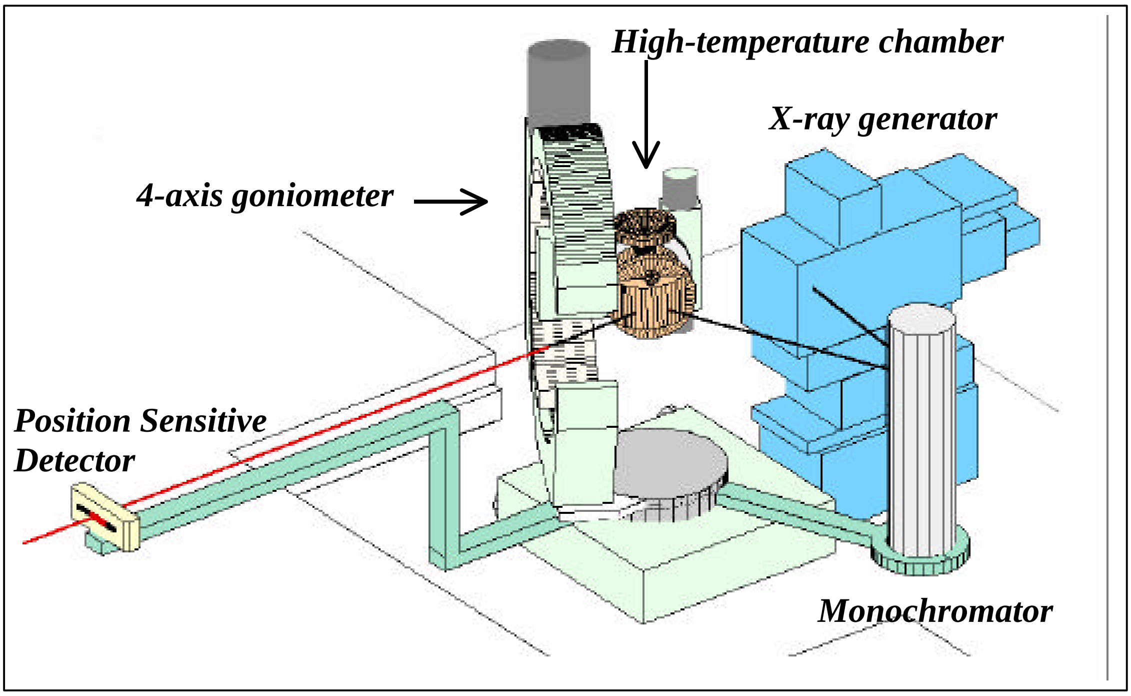

Fig. 1 – Schematic representation of the Hotbird Diffractometer. Both single and polycrystalline materials can be studied in vacuum and at high temperature (1400 ºC).

(*) See also the communication by *M. van Overveld et al.* in these proceedings.
(**) **Superalloys** are Ni base alloys, particularly successful owing to their outstanding performance in high temperature applications (> 1100 ºC) in the aeronautical industry.

The double-crystal X-ray diffractometer *Hotbird* is a being designed using a Computer Aided Design (CAD) in Three Dimensions to allow an easy correlation of the different components in space. Two-dimensional drawings are also being produced for the construction of components at the machine shop.

The diffractometer is being installed at a 18kW *rotating-anode X-ray generator*, *UltraX* from Rigaku, with two beam sources (line or point focus). The system has the following main components:

- two goniometers will be available, one for each generator source. One dedicated to residual stress measurements and another to perform high-resolution measurements. A rendered image of the latter is shown in Fig. 1. This goniometer will be allowed to move on top of four *'air pads'*.
- a computer controlled 4-axis goniometer (step resolution 0.001º) with a X,Y,Z stage to perform adjustments of the sample and perform scanning procedures across the sample.
- two stainless steel *high-temperature chambers* are being projected and manufactured (one for each goniometer). The furnace has a 400W power source to allow studies up to 1400ºC. A panoramic, low absorption, Be-window (water cooled) allows the alignment of single crystalline samples even at high temperature.
- *copper* and *molybdenum* anodes are available ($K\alpha_1$ and $K\beta$) with 1.4 and 0.7 Å wavelengths.
- monochromatic radiation will be selected by flat *Ge (440)* and *Si(444) monochromators* mounted on a three axis goniometer. A very high resolution 4-crystal monochromator is also planned.
- a *linear position sensitive detector* with its dedicated electronics will allow the collection of a full Bragg peak without 2θ scanning. The smoothness of the detector 2θ movement is guaranteed by an *'air pad'* system that keeps the detector levitating above the supporting table.
- a *high vacuum system* composed of a Turbo molecular pump connected directly to the chamber and a membrane pump.
- an exterior shielding with a steel structure and lead glass windows will protect users from hazard radiation.

References

[1] A.D. Sequeira and J. Bressers, *The Evolution of the Residual Stresses of CoNiCrAlY Coated Superalloys upon Thermo-mechanical Fatigue.* To appear in ***Materials Science Forum*** (1998).

[2] A.D. Sequeira, H.A. Calderon and G. Kostorz. *The temporal evolution of a bimodal distribution of g' precipitates in Ni-Al-Mo influenced by coherency strains*, in Thermodynamics and Kinetics of Phase Transformation, edited by J.S. Im, B. Park, A.L. Greer, G.B. Stephenson (***Mater. Res. Soc. Proc. 398,*** Pittsburgh, PA, 1995), 483-488.

[3] A.D. Sequeira and J. Bressers, *The Evolution of the Microstructure and Crack Propagation on* ***CoNiCrAlY Coated Superalloys upon Thermo-mechanical Fatigue.*** *EuroMat98.*

Communication to: *11th National Physics Conference*, Portuguese Physical Society (1998) 473-474.

DIDE – The New Neutron Diffractometer of ITN

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A new neutron diffractometer, DIDE, is currently under construction at ITN. DIDE is a two-axis powder diffractometer designed to allow various instrumental set-ups. DIDE will be equipped with a focusing monochromator and with a multidetector covering an angular range of 80^o with an angular resolution of 0.1^o. A range of different source-monochromator and monochromator-sample collimations, together with two possible choices of monochromating crystals and various monochromator take-off angles will allow the optimization of the instrument set-up for different studies and sample types.
Information is given about the design options and the present state of the construction work. The initial set-up and the predicted performance are presented. Research work with DIDE is addressed.

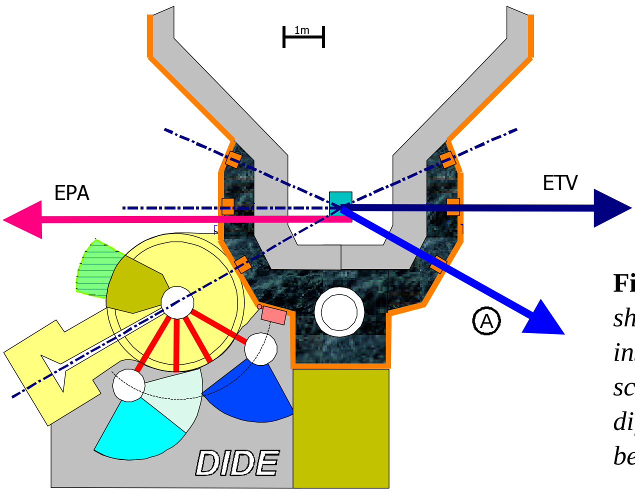

Figure 1 – *Schematic view of the RPI pool showing the position of the instruments currently installed and under installation:* **EPA**-*Small-angle scattering spectrometer;* **ETV**-*Time-of-flight diffractometer;* **A** – *multiple use beam tube (mainly beam modeling);* **DIDE**-*Two-axis diffractometer.*

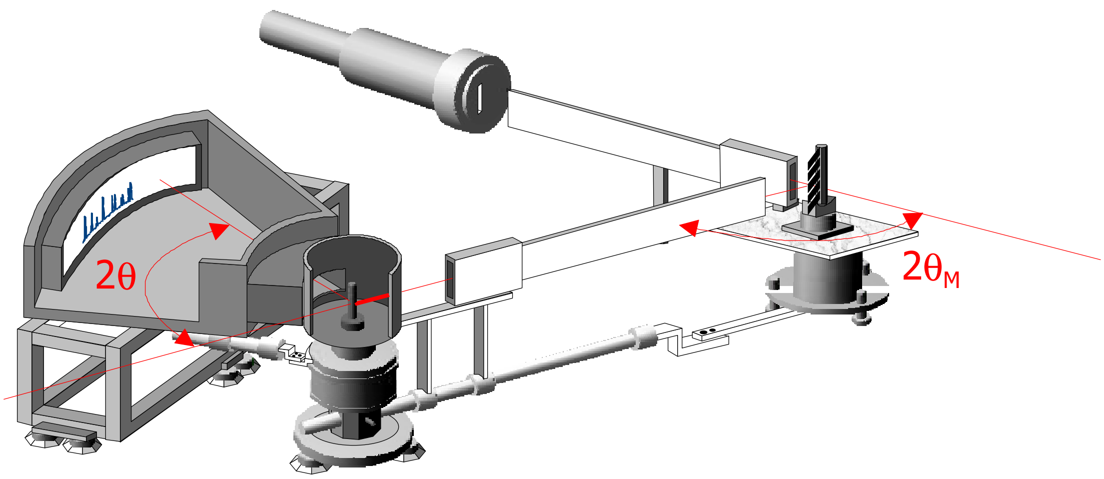

Figure 2 – *Schematic representation of the beam line of the diffractometer DIDE.*

Oral communication to the 11th Nat. Physics Conf. (1998), Maia, Portugal.

Current Work

Two-Axis Diffractometer DIDE

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A *two-axis diffractometer* to carry out structural studies in crystalline powder samples is under construction at ITN. It will be installed at beam port E1 of the Portuguese Research Reactor (RPI).

In 1998 the design study of the instrument was concluded. Different instrument components have been either built or purchased and the installation report has been prepared. Installation will start as soon as the assessment of the safety committee of the reactor is delivered.

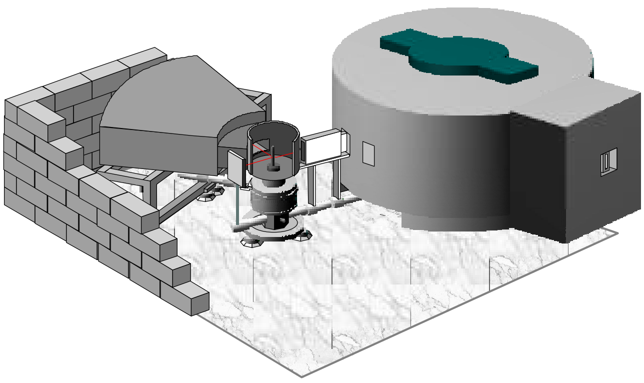


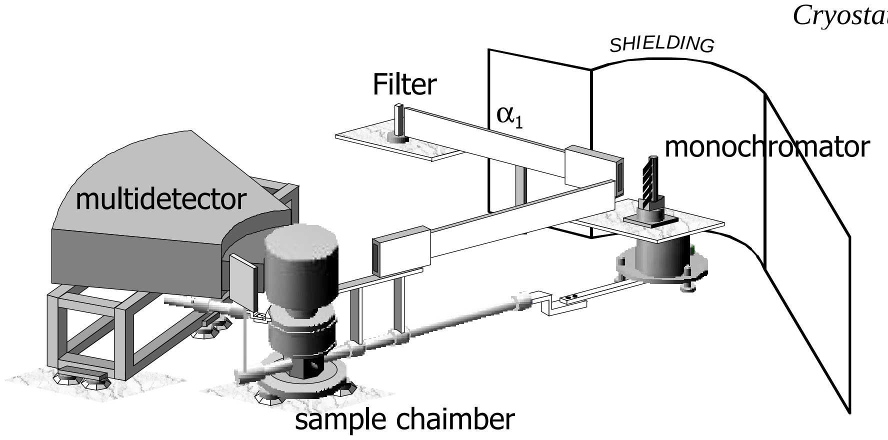
__Fig__. – Schematic views of the instrument (top) and of the beam-line (bottom).

Monochromator

Vertical focusing; two possible sets of crystals;
at start HOPG (002) – 11 crystals 60x12.5 mm^2.

Take-off-angles

25^o-65^o; 85^o-105^o
a_1 : open (40'); 20'
Beam-size at sample: *5x2 cm^2*
2q : *5^o-160^o*
detector:
BF3 multidetector
angular range 80^o
angular resolution 0.1^o
radius of curvature 1.51 m
Sample environment:
Cryostat



The Small-Angle Neutron Scattering Instrument — EPA

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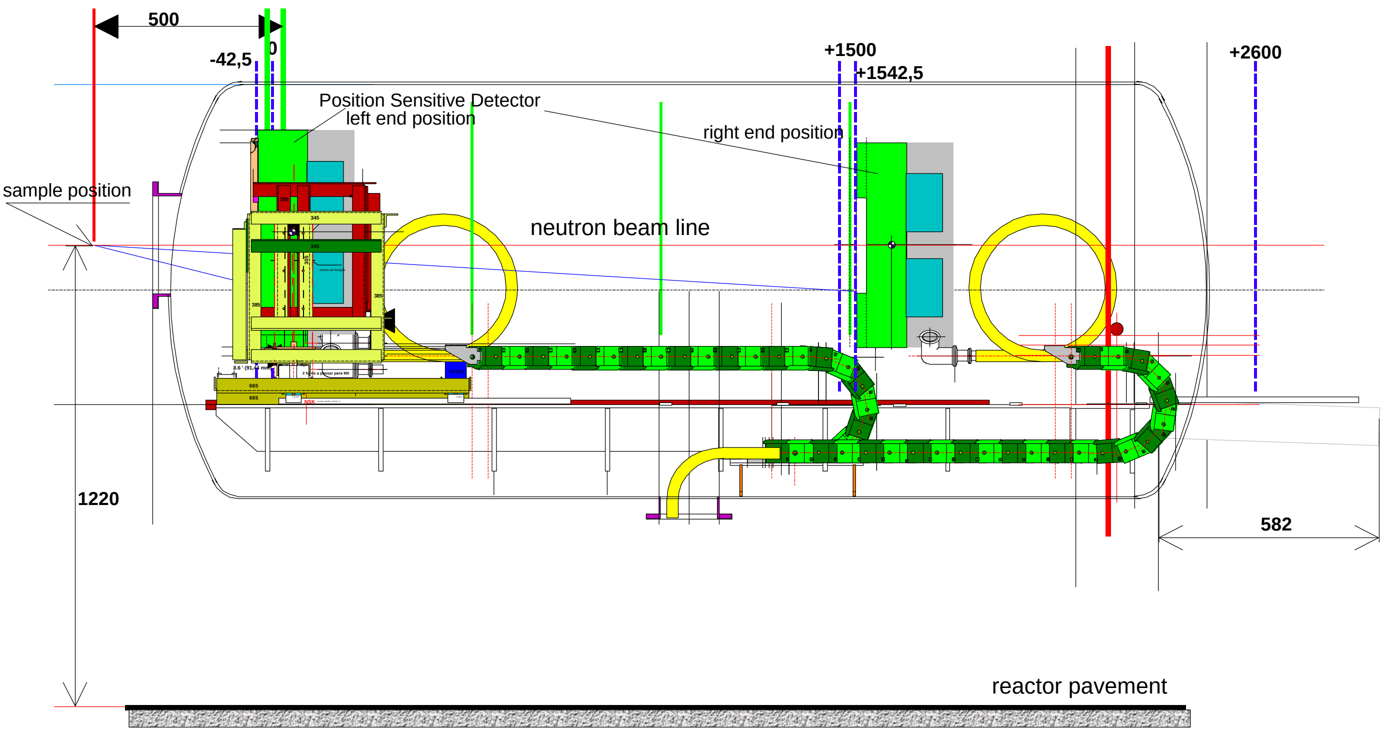
The EPA instrument has been designed using optimisation criteria developed at ITN for installation at the Portuguese Research Reactor tangential beam tube. Most mechanical components have been constructed at the ITN's workshops; the 2D-position sensitive detector and the neutron velocity selector were purchased. The detector chamber was fabricated by a national company.

In the year 1998, the standard testing and ageing procedure of the neutron velocity selector was successfully carried out. The detector carriage was designed and the mechanisms associated with the movements of the detector and the carriage were selected and purchased. The installation's technical report for safety evaluation purposes was prepared and transmitted to the reactor authorities.

Currently permission is awaited to start the spectrometer's installation at the reactor.



Schematic representation of the EPA detector chamber showing the extreme detector positions, the detector carriage and the cable movement.

Development of a Software Package for Remote Control and Data Acquisition from the Hotbird X-ray Diffractometer

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One of the particularities of the Hotbird diffractometer is that it is being projected, built and installed from scratch. This implies necessarily the development of all the facilities necessary for its functioning, that are assumed as-granted in a commercial instrument.
The aim of the current study is the development of an intelligent remote control system for the Hotbird concerning six main aspects: 1) Setting the values of the sample goniometer of four rotation axis (θ,ψ,ϕ and 2θ) and two three 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 these activities and monitoring have to be performed, continuously and simultaneously, by a redundant system of two computers protected by a UPS.
This software package is being 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 will applications that perform bilaterally checks.