Condensed Matter Physics

Introduction

Progress is reported on the development of infrastructures for neutron beam work at the RPI research reactor. This includes progress in design and construction work of the Small Angle Neutron Scattering Instrument to be installed at the reactor tangential beam tube E2-D2, and the first steps of the new project of a two-axis diffractometer with focusing crystal monochromator (DIDE).
Progress in the project of a multi-purpose high-resolution X-ray diffractometer facility is also reported. This facility is primarily intended for the characterisation of microstructure and study of internal strains and residual stresses of, e.g. coated superalloy samples at high temperatures. The major financing entity of this facility is the Portuguese National Research Council.
Reference is made to the utilisation for training purposes of the Neutron Time-of-Flight Diffractometer for powder samples, ETV, with a software package for the treatment of data now operational. The diffractometer is installed in radial beam tube D3 of the RPI reactor.
Results of current research in the following topics are presented: dependence of the microstructure of silica-based vitreous materials produced by the alcoxide method on the main parameters of the production process; production and characterisation of colour centres in alumino-silicates; measurement and modelling of internal strains in Ni base superalloys; bound states of water molecules in concentrated solutions of ionic salts.
Current research interests of the Group's scientific staff cover a range of material systems whose study requires the utilisation of a variety of tools. Neutron scattering is only one of the techniques used and is currently complemented with a range of other techniques that use different radiation probes (e.g., electrons, X-rays, visible light) for microstructure characterisation as well as with the more conventional techniques used for determining sample bulk properties.
For historical and objective reasons, low energy neutron scattering occupies a special place in current and planned activities of the Group, primarily due 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 considered a strategic aim to implement 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. As reported, several joint research projects in the indicated topics 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.

Research Team

Researchers –	5	(5PhD)
Research Students –	4	
Undergraduate Students –	3	
Technicians –	1	

Publications

Journals –	4
Proceedings –	3
Special Publ. –	3
Internal Reports –	1
Conf. Commun. –	5

10^3 PTE

Expenditure:	**8.980**
Missions:	1.364
Others Expenses:	1.380
Hardware & Software:	817
Other Equipment:	5.419

10^3 PTE

Funding:		**21.597**
OE/ITN	OF	1.156
	PIDDAC	3.635 (1)
External Projects:	1996	53 (2)
	1997	15.503 (3)
Others:		1. 250

(1) Small Angle Neutron Scattering Instrument
(2) Funding not used in 1996
(3) 12.000 funding for PRAXIS XXI Project to start in Jan. 98

SILICA BASED VITREOUS MATERIALS

A SANS Study of $ZrO_2 \cdot SiO_2$ Gels

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Abstract
Small Angle Neutron Scattering (SANS) measurements have been performed to investigate the nanoscale structure of materials of the system $x ZrO_2 \cdot SiO_2$ with $x \leq 10$ mol%, at different processing stages. The materials were prepared by sol-gel using the alkoxides method, in strong acidic conditions. Samples were studied as xerogels heat-treated at 120º C and 850º C and as wet gels at gel point and after 4 hours ageing at 60º C. The samples showed extended linear chains ca. 10 nm long at gel point. The aged gel has a mass fractal structure with fractal dimension of ca. 1.8. The 120º C heat-treated xerogel shows homogeneous oxide regions with 16 nm average diameter and mass fractal nature. For the 850º C heat-treated xerogel the oxide regions average diameter reduced to about 13 nm and presented sharp and smooth surface, obeying the Porod law.

Journal of Non-Crystalline Solids **209** (1997) 143-148.

Microstructure of Silicate Gels by SANS

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[2]*Glass and Ceramics Engineering Dept., Univ. of Aveiro, 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 gels of the systems $xMO_2.(1-x)SiO_2$ with M = Ti, Zr and $x \leq$ 10 mol%, at different processing stages. The samples were prepared by the alkoxide route of the sol-gel process and were studied as xerogels heat-treated at 120º C and 850º C and as wet gels at gel point and after ageing at 60º C. The present work reports SANS results which relate to the investigation of gels of $xTiO_2.(1-x)SiO_2$ with $x \leq 6$ mol% and $xZrO_2.(1-x)SiO_2$ with $x \leq 10$ mol%, both prepared with pH~1;and SiO_2 prepared with different pH values.

Proceedings of the *IAEA Technical Committee Meeting on Neutron Beam Research,* Edited by F.G. Carvalho and F.M.A. Margaça, Lisbon, September 10-12, 1997, pp. 50-55.

Investigation of the Microstructure of Silica Gels using Neutron Beams

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Glasses are known to man since antiquity being produced by the melting of oxides abundant in nature such as those found in sand and ashes. Man has long since learned in an empirical way, to select, modify and produce materials needed in daily life. However, the understanding of the fundamental nature of materials - why they have certain properties and why given manipulations produce particular effects - has taken much longer to develop. In fact, Materials Science only progressed in a meaningful way in the last 50 years, due to new techniques, novel instruments and new theories. The key contribution to the understanding of materials was the discovery that they possess an internal structure or architecture that determines their properties. Today researchers and engineers cooperate to characterize materials and investigate their internal structure at different spatial scales, in order to develop new materials and new process technologies.
Glasses produced by the novel sol-gel process are introduced while the importance of neutrons for the determination of the materials structure and the characterisation of the samples fabricated is emphasised. The process allows the preparation of materials with high purity and homogeneity at relatively low temperatures. Properties of the final product strongly depend on the processing conditions (composition and concentration of reagents, water content, pH, temperature and heat treatment). Completely different microstructures (at the nanometer scale) can be obtained by changing the process parameters, in particular, pH. This was observed using Small Angle Neutron Scattering, which has proven to be a most suitable technique to investigate the formation of the oxide network, at that scale, by measuring samples in different process stages.
The work reported is a co-operation between the Glass and Ceramics Dept. of Aveiro University and the Dept. of Physics of the Nuclear and Technological Institute.

Communication to: 1st National Meeting of the Portuguese Glass Association, "*The State of Glass in Portugal*", Marinha Grande, June 27, 1997 (in Portuguese).

Current Work

Microstructure Investigation of Silicate Materials

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[2]*Glass and Ceramics Engineering Department, University of Aveiro, 3810 Aveiro, Portugal*
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Samples of the systems xMO_2 (1-x)SiO_2 with M=Ti and Zr and x in mol%, have been prepared by sol-gel (alkoxides method) in the Glass and Ceramics Engineering Dept. of Aveiro University, and characterised by conventional techniques, including SEM, DTA, and X-ray diffraction. The sample structure at the nanoscale and the properties of the final product strongly depend on the processing conditions. Small angle neutron scattering (SANS) and positron annihilation spectroscopy (PAS) are used to gather information at the nanometer scale. Results obtained so far with these techniques have been reported in several papers.
SANS measurements were carried out at the Orphée reactor, in Saclay (one-week beam time at PAXE spectrometer). Certain samples were also measured by PAS at Sofia (Physics Department of Sofia University) to obtain complementary information, namely, to resolve the smaller pores.
Part of the SANS results were reported at the IAEA Technical Committee Meeting on Neutron Beam Research, held in Lisbon, September 10-12, 1997. Two papers will shortly be submitted for publication.

HIGH TEMPERATURE STRUCTURAL MATERIALS

Anisotropic Small-angle Neutron Scattering Patterns from Single-Crystalline Materials

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[3] *Department of Solid State Physics, Risø National Laboratory, DK-4000 Roskilde, Denmark*

Abstract
Nickel-base alloys, especially the so-called superalloys, are particularly successful materials in high-temperature applications. The high performance of these and other alloys is often due to the presence of an ordered phase of ordered coherent precipitates embedded in a disordered matrix. These submicron precipitates act as strong obstacles to dislocation motion, hindering plastic flow and thus giving rise to the increased strength of the alloy.
An isotropic distribution of spherical precipitates in a single-crystalline sample produces 'isotropic' SAS, i.e. the scattering intensity depends only on the modulus but not on the orientation of the scattering vector **Q** [whose modulus Q is given by $Q = (4\pi \sin\theta)/\lambda$, where λ = wavelength of the incident radiation, θ = half the scattering angle]. In Ni-base superalloys the precipitates (γ') are usually cuboidal owing to a finite lattice mismatch δ relative to the matrix [$\delta=(a_{\gamma'}-a_{\gamma})/a_{\gamma}$, where a_{γ} is the lattice parameter of the matrix (γ)], and the strain fields around the precipitates induce long-range interactions between them. Under the influence of these strain fields the precipitates tend to align along the soft elastic directions of the matrix, developing strong distance and orientational correlations, see e.g. (Sequeira *et al.*, 1994). The corresponding SAS is generally highly anisotropic, i.e. the scattering intensity depends also on the direction of the scattering vector.
From the analysis of two-dimensional (2D) SAS patterns it is possible to extract important information on the evolution of the morphology and on the three-dimensional spatial arrangement of the precipitates from the early stages of decomposition. The quantitative data analysis of anisotropic data is not straightforward, and standard methods of analysis, as they exist for isotropic systems (e.g. determinations of size distributions), are not available. Some attention has recently been devoted to this matter (Dubey *et al.* 1991, Fratzl *et al.* 1993, Vyskocil *et al.*1996, Pedersen *et al.* 1996). The authors (Sequeira *et al.* 1995a, Sequeira *et al.* 1995b, Sequeira *et al.* 1996) have recently published detailed information on the coarsening behavior of a bimodal distribution of γ' precipitates in highly strained samples of Ni-Al-Mo. Some of these results will be used here to illustrate the SAS data analysis.

J. Appl. Cryst. **30** (1997) 575-579.

Small-angle Neutron Scattering as a Tool for the Study of Decomposition Processes in Single Crystalline Superalloys

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Physics Department, Nuclear and Technological Institute, Estrada Nacional 10, P-2685 Sacavém, Portugal. http://newton.itn.pt/htsm

Abstract
'Isotropic' small-angle scattering (SAS), i.e. without azimuthal dependence around the primary beam, occurs only for specific configurations of the scattering objects if single-crystalline material is studied. In the case of decomposing Ni-base alloy single crystals, SAS signals are generally highly anisotropic.
From the analysis of two-dimensional SAS patterns, it is possible to extract important information on the evolution of the morphology and on the three-dimensional spatial arrangement of the precipitates from the early stages of decomposition. The real-space information obtained from transmission electron microscopy is an excellent complement to the reciprocal-space information extracted from SAS data. The complementarity of these two techniques offers a valuable approach to study precipitation phenomena.

Proceedings of the *IAEA Technical Committee Meeting on Neutron Beam Research*, Edited by F.G. Carvalho and F.M.A. Margaça, Lisbon, September 10-12, 1997, pp. 126-133.

Nanoscale Mapping of Internal Strains in Crystalline Materials by Convergent-beam Electron Diffraction

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

Abstract
One of the various techniques that may be used in a transmission electron microscope (TEM) is called convergent beam electron diffraction (CBED). This technique allows, among other things, the determination of lattice parameters with a very high precision. By moving the beam inside a certain phase or within coherent phases it is possible to map, at a nanoscale, the local strain fields inside single crystalline domains.
Origin of higher order Laue zone 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. 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 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.

This technique permits the imaging of dislocations containing both the direction and the magnitude of the Burgers vector.

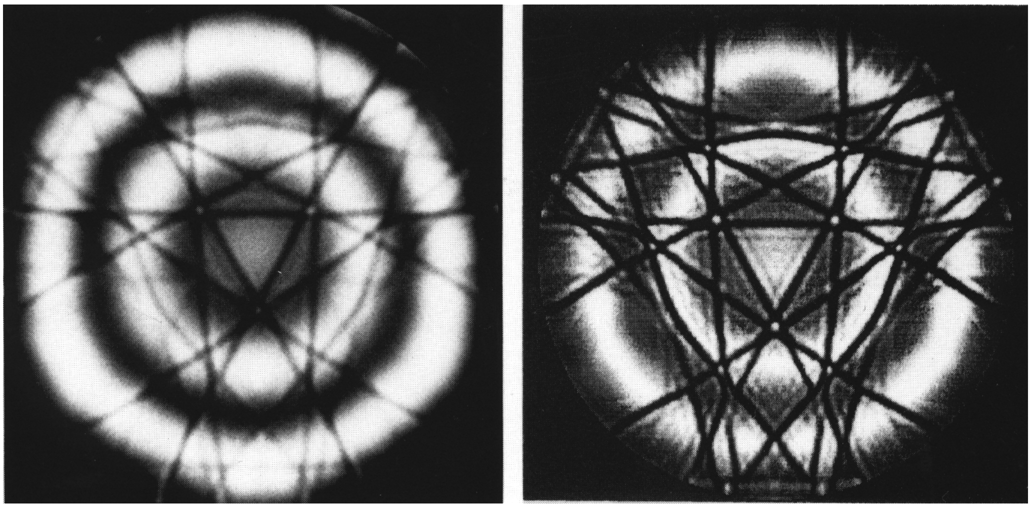

Figure – Convergent beam electron diffraction pattern in the [111] pole (a) of a Si standard. In (b) the corresponding simulation pattern is shown. Since the lattice parameter of Si is known the accelerating voltage of the electron microscope can be determined by fitting the experimental pattern. In the present case the determined value was 100.0 kV.

Local measurements of lattice parameters. A Philips EM400 electron microscope was used to determine the lattice parameter of the phases present by convergent-beam electron diffraction (CBED). The local character of this technique allowed 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 appear in *Materials Challenge* **12**, JRC Bulletin, European Commission, edited by E. Bullock (1997) (in press).

Imaging of Three Dimensional Properties of Cracks on CoNiCrAlY Coated SRR-99 using Scanning Electron Microscopy

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[2] *Institute for Advanced Materials, PO BOX 2, 1755 ZG Petten, The Netherlands.* http://newton.itn.pt/htsm

Abstract

Owing to the considerable improvement, in the last decades, of the properties of Ni base alloys and the design of turbine blades, the service temperature of jet engines kept increasing. A turbine rotor blade of a modern gas turbine engine experiences temperatures in excess of 1100^{o} C at its outer surface. Yet one aims still to increase it. The increase of the service temperature of an engine will improve its efficiency, which reduces fuel consumption and emission of pollutants. However, the increase of service temperature of the blades intensifies their oxidation with the consequent reduction of life. To counteract these effects modern blades have their surface protected with a *coating* with good oxidation resistance. However, in some cases a degradation of their in service performance is observed.

The most common mechanism of damage observed in these materials, when subjected to thermo-mechanical fatigue (TMF), is the occurrence of cracks. In general the coating has poorer mechanical properties than the substrate and is more prone to cracking. In this situation, the critical step that endangers the life of the component is the penetration of the substrate by cracks originated in the coating.

By means of electropolishing and/or electroetching it is possible to selectively remove specific phases making it feasible to study the three dimensional characteristics of a crack and its oxide envelope (see Figure).

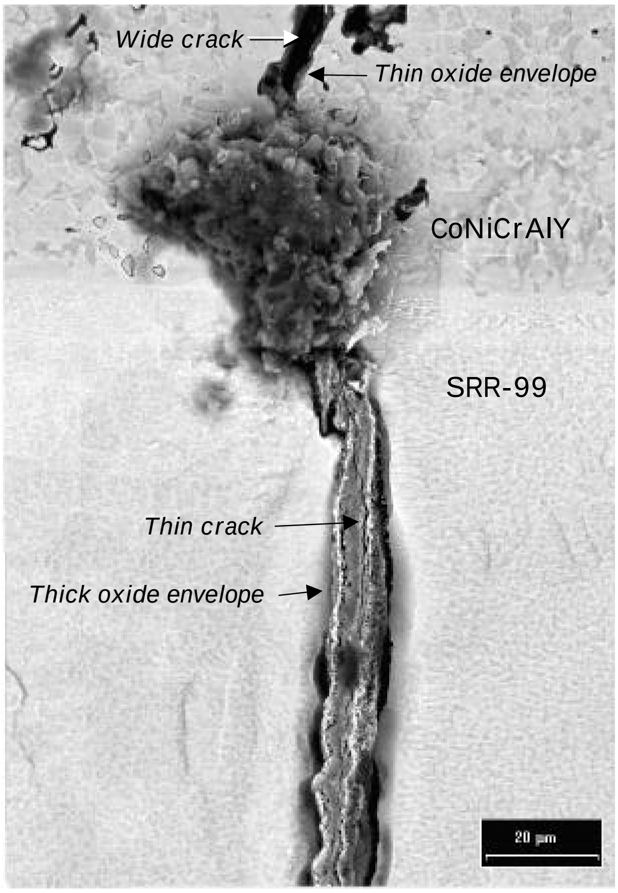

Figure – 3D view of the interface region of a crack and its oxide envelope. This crack was initiated at the surface of the coating from where the thick oxide layer was nourished with oxygen .

The morphology and the width the crack changes considerably from the coating to the substrate. Whereas in the former the opening of the crack is very wide and the oxide layer thin (less than one micron thick) in the latter the cracks are very narrow (a few hundred nm) and have a thick oxide layer (10 µm). In some cases the width of the crack changes quite dramatically at certain length intervals. This corresponds to the appearance of pores in the path of the crack. The intense local stresses associated with the pores are driving the crack's path. The crack is acting as a stress-relieving mechanism connecting consecutive pores as it progresses towards the interior of the sample.

To appear in *Materials Challenge* **12,** edited by E. Bullock, JRC Bulletin, European Commission (1997) (in press).

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

***A.D. Sequeira*[1] *and J. Bressers*[2]**

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[2] *Institute for Advanced Materials, PO BOX 2, 1755 ZG Petten, The Netherlands.* *http://newton.itn.pt/htsm*

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 (see Figure), 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.

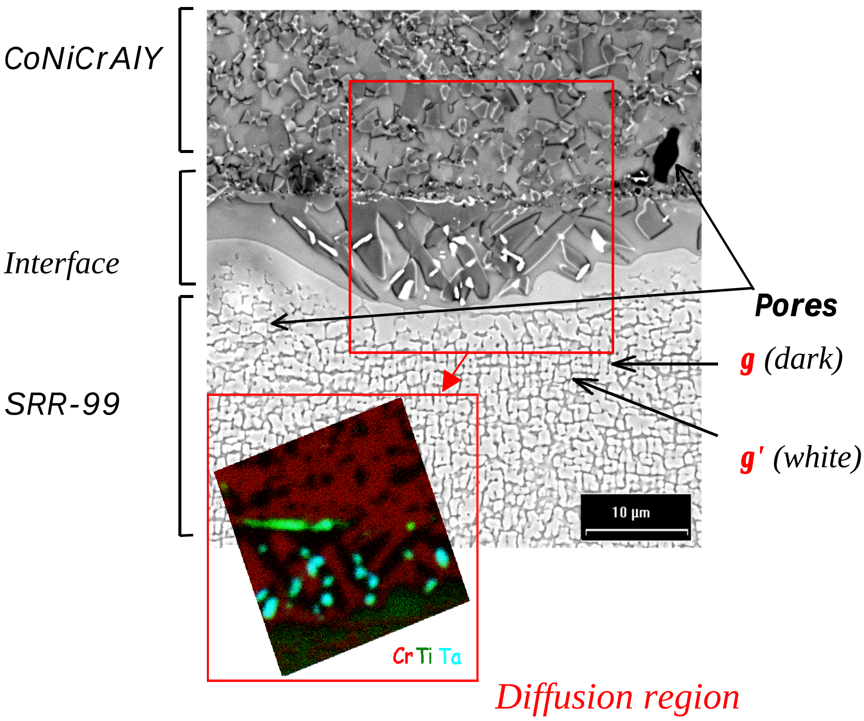

Figure – Back scattered electron images of the interface region of the as-received material. The inset represents a composed EPMA chemical mapping identifying the different carbides present at the interface region.

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.

Accepted for publication, **EuroMat98.**

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

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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 Δε. 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.

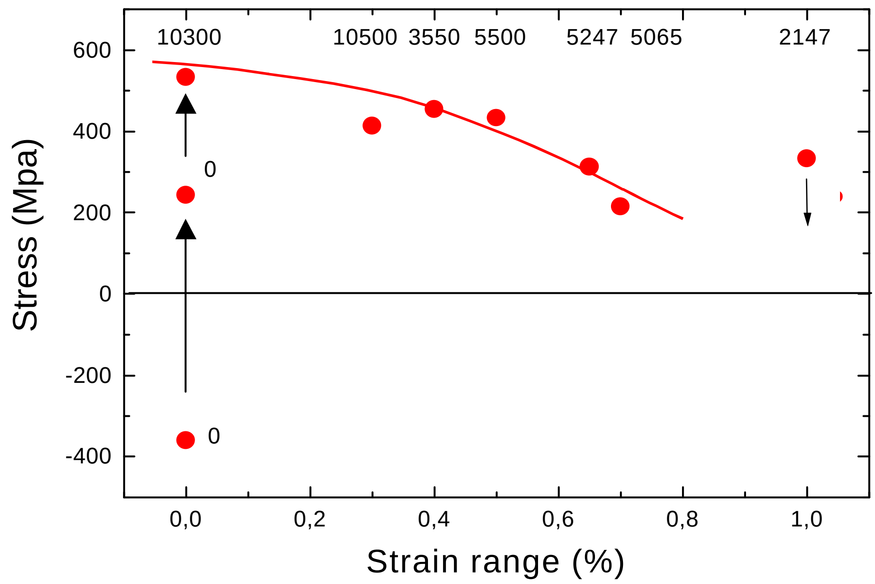

Figure – Residual stress dependence on strain range. Only results of out-of-phase test conditions (-135^o lag) and R= -∞. Cycle number is indicated on top.

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, σ(γ) = + 243 Mpa (see Figure). A detailed interpretation of the residual stress results is given.

To submit to *Materials Science Forum*. EPDIC-6 Budapest.

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.

To submit to *Materials Science Forum*. EPDIC-6 Budapest.

Current Work

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

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[1] *Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisboa Codex, Portugal*
[2] *Physics Department, Nuclear and Technological Institute, Estrada Nacional 10, P-2685 Sacavém, Portugal*

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 commercial coatings.

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

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Physics Dept., Nuclear and Technological Institute, Estrada Nacional 10, 2685 Sacavém, Portugal

One of the particularities of the Hot-bird 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 Hot-bird concerning six main aspects: 1) Setting the values of the sample goniometer of four rotation axis (θ,ψ,ϕ and "2θ") and two linear stages (x,y) 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 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.

AQUEOUS SOLUTIONS

The Structure and Dynamics of Concentrated Aqueous Solutions of Aluminium and Magnesium Salts

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[1]*Instituto Tecnológico e Nuclear, Estrada Nacional nº 10, 2685 Sacavém - Portugal*

[2]*Departamento de Física, Instituto Superior Técnico 1096 Lisboa - Portugal*

[3]*Centro de Física da Matéria Condensada (UL), Av. Prof. Gama Pinto, 2, 1699 Lisboa Codex Portugal*

Abstract

Raman investigations (1) of the structure of concentrated aqueous solutions of aluminium and magnesium inorganic salts demonstrated the existence in these solutions, of (relatively) stable cation hydrates. Later studies(2) suggested that a small isotopic shift of a polarised Raman band observed in the spectra of solutions of aluminium salts would be estimated by assuming a coupling between librational and vibrational oscillations of the coordinated water molecules. As librational motions are Raman inactive, inelastic neutron scattering of those concentrated solutions was investigated in the High Energy Transfer Spectrometer of the Rutherford Appleton Laboratory (Didcot, U.K.). The dynamic structure factor for the investigated solutions was obtained for values of the energy transfer up to 180meV and up to 300meV in different series of experiments. The interpretation of the scattering results is discussed and previous investigations (2,3) are analysed.

1. A. da Silveira, M. Alves Marques and N. Macias Marques, Mol. Phys., 1965, **9**, 271.
2. M. Alves Marques, M.A. Sousa Oliveira and J. Resina Rodrigues, J. Chem. Soc. Faraday Trans., 1990, **86**, 471.
3. K. Toukan, M.A. Ricci, S. Chen, C. Loong, D.L. Price and J. Teixeira, Phys. Rev. A, 1988, **37**, 2580.

Communication to: *IAEA Technical Committee Meeting on Neutron Beam Research*, Lisbon, September 10-12, 1997.

RADIATION INDUCED OPTICALLY ACTIVE DEFECTS

Current Work

Production and Characterisation of Colour Centres in Alumino-Silicates

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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 electron, γ-ray 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.
During 1997, the preliminary steps required to launch a project to study defects structures in topaz were taken. Samples originating from different extraction sites were made available. Tests were performed on some of the samples in order to assess their ability to become coloured upon γ-ray and neutron irradiation. In order to evaluate possible nuclear activation, the chemical composition of the samples used was checked prior to the irradiation experiments by means of non-destructive techniques (RBS and PIXE). Subsequent annealing of the irradiated samples was successful in producing stable blue colours. To prepare the neutron irradiations at the Portuguese Research Reactor (RPI), it was necessary to develop an irradiation device meeting the safety requirements of the reactor operation and allowing for temperature control of the sample environment. Due to the complexity of the gamma and neutron fields at the sample, the energy deposition in the irradiated materials was calculated using the Monte Carlo simulation technique - since the simplificative assumptions required by any analytical approach would entail the risk of misleading results. The MCNP [1] code was used, and the results obtained are summarised in a paper that will shortly be submitted for publication [2].
Preparation of the samples required for a systematic study was started.
Defects will be produced by gamma-ray, neutron, and ion-beam bombardment. The structure of the samples will be studied at Sacavém by RBS, RBS/channelling, X-ray and neutron scattering, and by spectrophotometry.

Collaboration is foreseen with the Physics Department of the University of Aveiro where facilities for the optical characterisation of samples exist.

[1] - Briemeister, J. F. (Ed.), MCNP - A general Monte-Carlo n-particle Transport Code, Version 4A,LA-12625-M,(1993).

[2] - Marques, C., Falcão, A.N., da Silva, R. C., to be submitted.

NEUTRON BEAM RESEARCH – GENERAL

Report on the Lisbon Meeting on "Neutron Beam Research"

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Abstract
The IAEA Technical Committee Meeting on "Neutron Beam Research", hosted by the Nuclear and Technological Institute, Sacavém, Portugal, was one of a sequence of specialized meetings dealing with the subjects of research reactor utilization and neutron beam applications in Science and Technology promoted by the Agency to help Member States utilize more effectively their research reactors and other resources. Invited speakers offered an overview of their special subjects emphasizing the importance of the neutron as a tool and its complementarity to other techniques. Aspects emphasized during the meeting and in the closing session dedicated to highlights and recommendations are reported.
Neutron techniques and their applications continue to evolve and to develop in research but also in areas of direct impact to wealth creation. To keep the use of neutrons at its present level and more importantly to further promote neutron techniques relies most certainly on the availability in a long-term perspective of an international network of intense neutron sources but also on the efficient use of national small and medium flux sources. There are specific uses in view of which these sources have a high potential, namely , education and training of young researchers in the field of neutron techniques and new instrument development, among others.
The capability of existing facilities (primary source plus instruments) to generate data can still be improved through design optimization and the introduction of technologically advanced components (supermirrors, multidimensional detectors).
To become a user facility a neutron centre must provide adequate sample environment, instrument maintenance, and facility operation schedule and management practices.
A certain number of recommendations were made concerning peripheral and emerging centres, e.g. to support the exchange of scientific visitors between major laboratories and developing centers; facilitate information exchange on neutron work via the Internet. Also the interest of building a network among small laboratories to benefit from a possible complementarity of experience and skills was mentioned.

Neutron News, (in press).

IAEA Technical Committee Meeting on Neutron Beam Research: Summary of the Proceedings-Reports of the Chairs of the Topical Sessions

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[4]*Riso Nat. Laboratory, Condensed Matter Physics* **&** *Chemistry Dep.,4000Roskilde, Denmark*
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Abstract
The Lisbon Meeting on “Neutron Beam Research” was undertaken by the International Atomic Agency in the framework of a regular series of “Technical Committee Meetings”. It was organised locally by the Nuclear and Technological Institute (Sacavém) and brought together 41 participants from 20 countries. The meeting highlighted results obtained by neutron techniques in various fields in oral presentations and discussions. In the closing session summary reports were presented by the Chair persons of the seven topical sessions and a general discussion took place centred around the major aim of the meeting, namely, to stimulate and improve the utilization of existing neutron sources, in particular, low- and medium-flux national sources.

Proceedings of the *IAEA Technical Committee Meeting on Neutron Beam Research*, Edited by F.G. Carvalho and F.M.A. Margaça, Lisbon, September 10-12, 1997, pp. xix-xxvii.

Neutron Beam Work at Sacavém and the ITN Group of Condensed Matter Physics

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Abstract
Aims, strategy, current work and future prospects of the ITN Condensed Matter Physics Group are reported. The utilization of low energy neutrons as a probe to study the structure and dynamics of material samples is the main common feature of the experimental approach to the different problem areas in which the Group —formerly named Neutron Scattering Group — has been involved[1-6].
The Group has commissioned a Neutron Time-of-Flight Diffractometer and is preparing the installation of a Small Angle Neutron Scattering Instrument at the ITN 1 MW Swimming-Pool Research Reactor RPI (max. $\Phi_{th} = 2x10^{13}$ cm^{-2} s^{-1}). DIDE, a Two-Axis Diffractometer with a "banana" multidetector is currently being designed. The Hot-Bird, a multi-purpose high-resolution high-temperature X-ray Diffractometer is in construction. This facility is primarily intended for the “in situ” study of the development of internal stresses in metal alloy samples at high temperature.

The Group aims at building up an adequate infrastructure of experimental facilities for neutron beam work at the RPI reactor to be used in research and for graduate and post-graduate training. The relatively low flux of the reactor limits the range of problems that can be fully investigated locally. The normal development of the Group's activity requires therefore a strong interaction with the international neutron scattering community and the possibility of accessing intense neutron sources.

Proceedings of the *IAEA Technical Committee Meeting on Neutron Beam Research*, Edited by F.G. Carvalho and F.M.A. Margaça, Lisbon, September 10-12, 1997, pp. 159-162.

Neutron Scattering Instruments at the Portuguese Research Reactor

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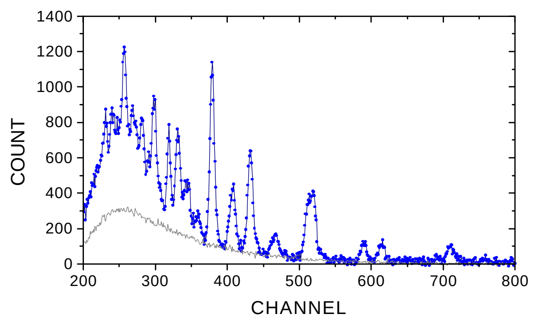
Abstract
It became recently possible to perform neutron diffractometry in Portugal using the RPI Research Reactor. A new Time-of-Flight Diffractometer (ETV) has been commissioned in May 1997 (see figure). The installation of a Small-Angle Neutron Scattering instrument, EPA, is under way. Test measurements are being scheduled to be performed during the second half of 1997. The design study of a Two Axis Diffractometer is starting now, the instrument being expected to be operational by late 1998. The technical specifications of the three instruments are presented, and perspectives for their utilization are discussed.



Raw spectra of a 1.5 cm^3 YBCO powder sample, and a Vanadium calibration sample obtained with the Time-of-Flight Diffractometer ETV.

Communication to: *Seventeenth European Crystallograpic Meeting ECM-17*, Lisbon, August 24-28, 1997.

Notes on the Neutron Scattering Scene in Portugal

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Abstract
The RPI research reactor at Sacavém near Lisbon is operating at 1MW. The instrument suite is partly commissioned and partly in the build up process. The group operating these instruments consists of eleven persons including technicians and students.
The national user community consists of about 30 people which use the neutron sources at Saclay, Risø, ISIS and ILL.
For 1998 a user meeting is planned in order to discuss the use of the national and foreign neutron sources and to organise an independent neutron scattering society or a largely independent branch of the Portuguese Physical Society.

Communication to the *8th European Neutron Scattering Association Committee Meeting*, Delft, Holland, December 8-9, 1997.

INFRASTRUCTURE DEVELOPMENT

Current Work

The Small-Angle Neutron Scattering Instrument — EPA

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Progress is reported in system and component design, construction and testing for the EPA SANS instrument.
The tank to house the Position Sensitive Neutron Detector has been commissioned. Construction was subcontracted to a manufacturer in Vale de Cambra, Northern Portugal. A first draft of the structure intended for holding and positioning the detector inside the tank was completed. The mechanisms that are necessary to move the detector were specified and purchased. The detector carriage is currently being designed. The detector has three movements. Positioning along two axis will be remotely controled. The carriage is to be constructed at the main workshop. Also driver modules and their computer interface will be developed and produced locally.
The sample chamber design was completed. Construction is under way at the ITN workshop. The chamber is designed to house a 5-sample holder and sample changer in a vacuum. This is equipped with a heating element for measurements above room temperature up to ca. 80ºC. Positioning of the samples in the beam is automated.
The neutron velocity selector was the object of refurbishment work. The 50 mm thick steel base plates were removed, cleaned and protected against corrosion. Their surface in contact with ball bearings was polished and then covered with plates of a harder steel. A new angular position sensor currently under test was purchased and installed. Also the velocity selector's electronic controller unit was tested and made operational.

Two-Axis Diffractometer DIDE

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Following the shut down of the Siloé reactor, operated by CEN Grenoble, of the French CEA, some of the neutron scattering equipment that was installed in the experimental hall of Siloé became available. In the framework of a co-operation agreement between CEA-DSM and ITN, currently being prepared, the multidetector that equipped Siloé's D5 diffractometer was made available to ITN for the purpose of installing a two-axis diffractometer in a radial beam channel of the Portuguese research reactor RPI. The detector is a BF_3 filled multidetector, constructed during the 80's at ILL. It covers an angular range of 80º with an angular resolution of 0.1º. Presently the detector is in store at the LLB in Saclay.
The present state of the detector was assessed in November/December in collaboration with the LLB. Both the gas filling and the electronics were tested. Damaged circuits were replaced or repaired. A design study of the new instrument was then undertaken bearing in mind that the instrument should be flexible enough to allow for future upgrade and optimisation for different kinds of studies. The full height of the available beam will be used by means of a vertically focusing monochromator. Two monochromating crystals, several possible take-off-angles and collimations will provide accessibility to a large *q*-range and different experimental resolutions. The installation set-up will favour intensity rather then resolution, and will leave open the possibility of future upgrades.

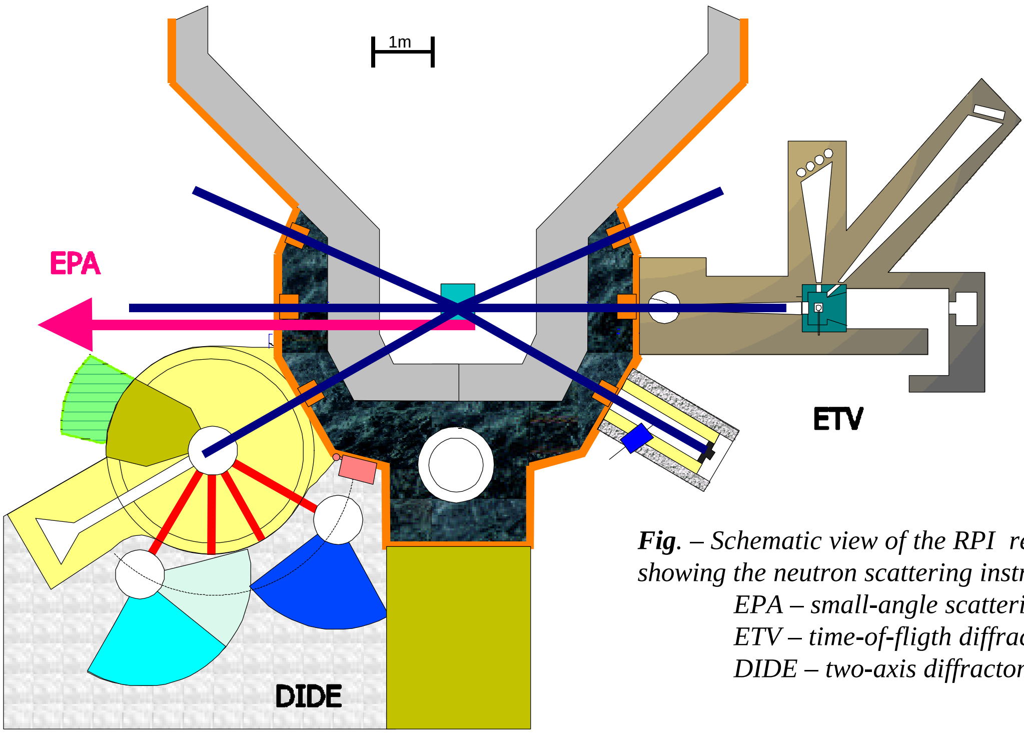

Fig. *– Schematic view of the RPI reactor hall showing the neutron scattering instruments*
EPA – small-angle scattering
ETV – time-of-fligth diffractometer
DIDE – two-axis diffractometer

High-Resolution and High-Temperature Double-Crystal X-ray Diffractometer for *in-situ* Studies on Crystalline Materials - The Hot-bird

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A *high resolution X-ray diffractometer* to carry out diffraction experiments *in situ* at high temperature is being built and installed. This technique has recently risen much interest in

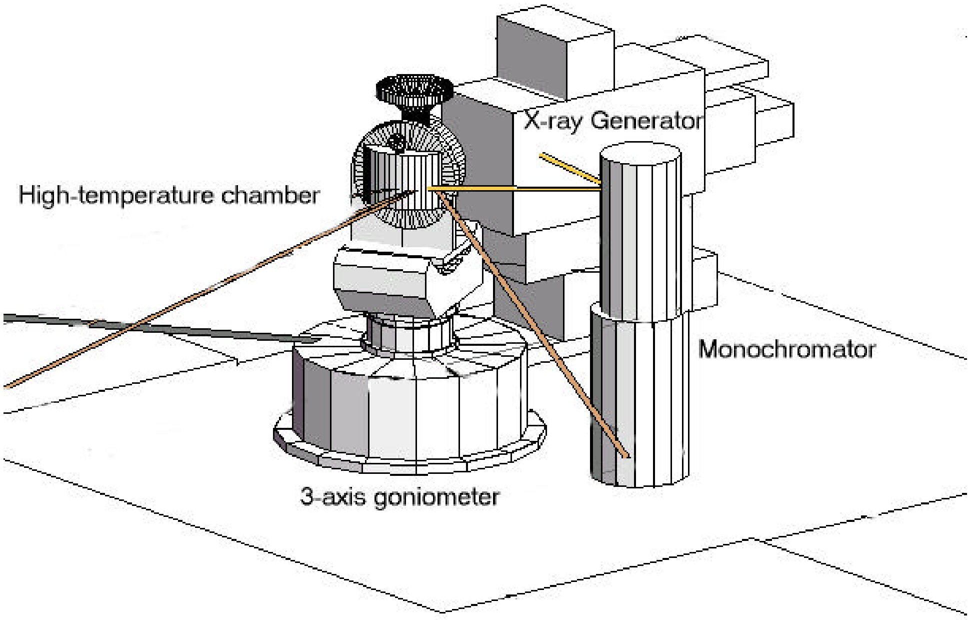

Fig. 1 - Schematic representation of a section of the of Hot-bird diffractometer. Both single and polycrystalline materials can be studied in vacuum and at high temperature (up to ~1300 ^{o}C).

numerous research groups, namely, to determine internal stresses in ceramics and *superalloys*[(*)]. Such an instrument is rare and is not commercially available.

The instrument will be used for the characterization of high-temperature properties of high temperature structural materials, e.g. superalloys. The instrument will be particularly suited to perform determination of residual stresses, determine lattice parameters with high resolution, to observe in-situ the formation of intermetallic precipitates in implanted metals and semiconductors.

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 foreign teams and the training of young scientists.

The diffractometer has the following main components: high-temperature chamber, projected by the team and manufactured locally, a position sensitive linear detector with its dedicated electronics and a high vacuum system, and is being assembled by the team.

[(*)] **Superalloys** are Ni base alloys, particularly successful owing to their outstanding performance in high temperature applications (> 1100 ºC) in the aeronautical industry.

Time-of-Flight Diffractometer ETV

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In the course of 1997 the data treatment software package of the time-of-flight diffractometer was installed. This was done in collaboration with Dr. Robert McGreevy, of Studsvik, Sweden, during a one-week visit financed by the IAEA in the framework of a technical co-operation project intended to provide external inputs for the development of local neutron beam work.
The instrument is essentially meant for training and educational purposes in general. This has started in 1997. The ETV was used for experimental work complementary of introductory lectures to neutron scattering in a collaboration with the Physics Department of the Faculty of Sciences of Lisbon University. It was also used to demonstrate neutron diffraction to undergraduate students from the Engineering School of the Technical University of Lisbon, and from the Physics Department of Aveiro University, Northern Portugal.