State of the art of XRD and ND technology in Pisa at 2006
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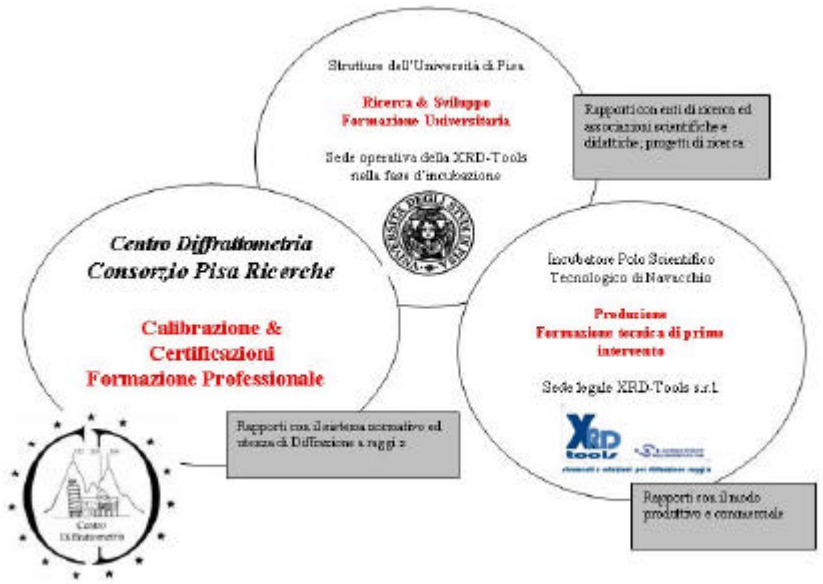
Since the 60's in Pisa the study of X-Ray diffraction had an intense applicative development in the field of chemistry and crystallography for the study of minerals. An X-ray lab was created in the former Mineralogy and Petrography Institute, dedicated to the mineralogical analysis through X-Ray.
More recently, at half of the 80's, the Department of Earth Science ciontributed to the advances in data reporting and interpretative methods of X-Ray Diffraction (XRD) as a consequence of the introduction of computers in the interpretation of XRD patterns.

In the 90's, as a consequence of the scientific results obtained, some normative gaps were identified; methods were implemented for the identification of the characteristics curves of diffractometers, collaborations with researches institution and industries were started that brought to identify new prototype and new applications for XRD. In particular here mention the direct use of an XRD instrument to be used on the site of components in service.
In the last ten years the experience in Mobile XRD (MXRD) suggested to trasfer to Neutron Diffraction some of the advances made. This last development still requires specific experiments which have a great potential impact on sectors involoved in heavy metallurgy.

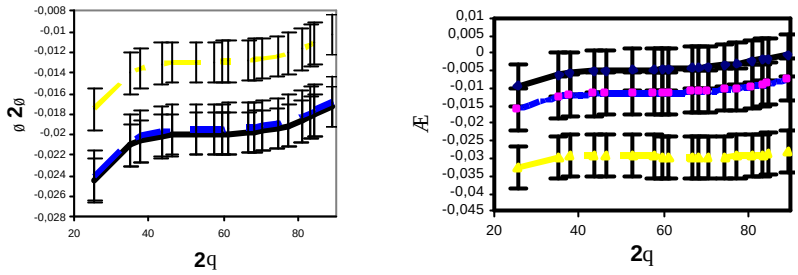
A system in synergy

Pisa offers some interesting perspectives thanks to the creations of favourable synergies among different institutions, as described in the following graphic.



1. the project "Centro Diffrattometria" or better "Diffraction Measurement and Testing Centre" begun in 1994 in Consorzio Pisa Ricerche. The meaning is unequivocal and summarized in the Centre's logo, where the "C" and "D" characters sorround one of the most famous monument in the world. Such a monument is the finger print of Pisa and the diagram above ideally represents the crystalline excellence of the condensed matter fron XRD traces. In collaboration with CNR, Univ. of Pisa and Alenia have been made the first XRPD non destructive measurements tests. Then, in collaboration with the Italian national group of standardisation, a research started for the calibration of XRD instruments. This research is

known at the highest international levels (as ICDD). From the previous activities come out the possibility to obtain characteristics curves of diffractometers and from those the calibration of measures on specific materials.



2. The 3th December 2003 XRD-Tools s.r.l. was born as the academic spin off addressed to the production of devices (as main line of business); the decision was the follow up from the researches developed in the Univ. of Pisa, in collaboration with said Centro Diffrattometria and a generous support from ISPESL, the institution of Italian Health Minestry who survays the safety on working places. The implemetation of the first prototype was made possible. The second prototype of mobile diffractometer is going to be available at short under the warranty of an Italian Finacial Institution. Good results have been achieved in measures of mobile diffractometry on precious and refined materials as "brochette" of "Museo degli Argenti" di Palazzo Pitti in Florence

3. the 10th October 2004 was created the of Research & Development lab for Diffraction RX (R&D-XRD) in the Univ. of Pisa. (this is a branch of the ancient "X Ray lab" of the former Institute of Mineralogy and Petrography. The R&D-XRD lab inherits the long work on methodological and development research done in the last tenth years of the passed century. It has already largely contibuted to the success of the interpretation of very difficult XRD obtaine from MXRD (e.g the patterns from te "brocchette" of Museo degli Argenti, the surface of Titanium diskettes for biomedical application and for the steel and alloys or industrial applications.

Developments to accelerate

The introduction of new innovation in XRD requires an increasing consciousness in market (even the training in the industries). For this reason the synergies that are in Pisa identify the institutions and the skills to define a coherent and reliable frame.

The XRD characteristic techniques are limited by the ability of penetrating materials. The XRD is an useful technique for surface analysis (not over a few hundreds of microns). Instead of XRD, the Neutron Diffraction is not able to analyse the first layers but the deeper one of the material. The problem to overcome is the flux of neutrons able to interact with materials lattices (thermal neutrons) and to be detected. This flux of neutrons is available at High Flux Reactors (HFR). Today there is the possibility to build a NDmeter that works far from HFR (exists a patent at the stage of PCT review). Specific technological implementation is still required to verify the real potentiality and economical benefit for such device. When it could be possible to demonstrate that XRD and ND can be concentrated into one instrumentation usable far from HRF, the economical potentiality of the instrument will have an increasing for application in aeronautic and space field. This implementing research could take probably one year.
In both cases, the sensibility of the analysis to the variation of tensions, seems encouraging for a research in metrology sense. Follows some figures that summarize the evolution of the technology

state from the first experiments done in collaboration with CD-CPR, Univ. of Pisa, Alenia and then ISPESL, XRD-Tools.

Fig. 1 (on the left)- XRD analysis performed at around the 1996 using a lab diffractometer; this devices was rearranged for non destructive analysis on the line welding which covered the maximun circle of a spheric satellite tank provided by Alenia.

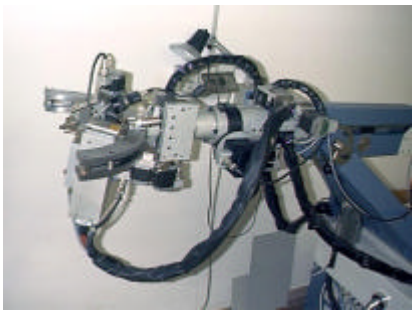


Fig. 2 (on the right)- Prototype of X ray diffractometer realized by Univ of Pisa in collaboration with ISPESL. It's the first mobile diffractometer equipped with height freedom degrees and pointing devices controlled at distance through computer. Within the X-ray adopted optics it gives results equivalent to lab equipments. Tests on different types of materials give good results. Respect the lab diffractometers there is no need to link mechanically the goniometer centre to the specimen holder. The configuration is a virtual centre diffractometer. (Patent just published and at the nationalization stage).

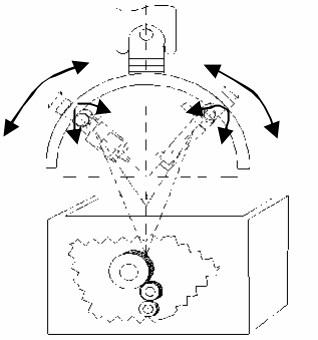


Fig. 3 (on the right)- It is an evolution of the former diffractometer in which the addition of two further freedom degrees permits the rotation of detector and source. The adoption of parallel optics devices and suitable rotations dimensioning, controlled through software permits to analyse hidden objects without previous disassembly. It's a device with variable virtual centre (Patent under PCT review).

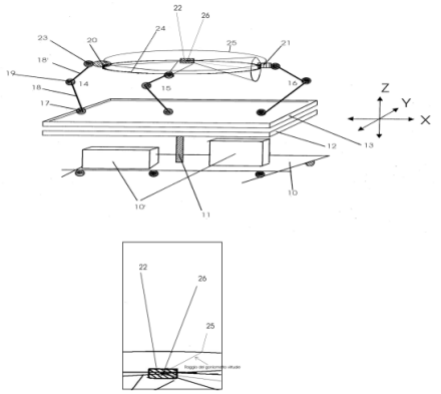
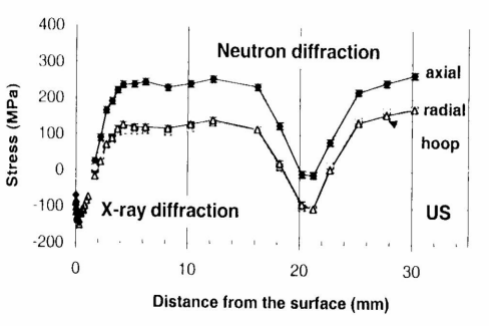
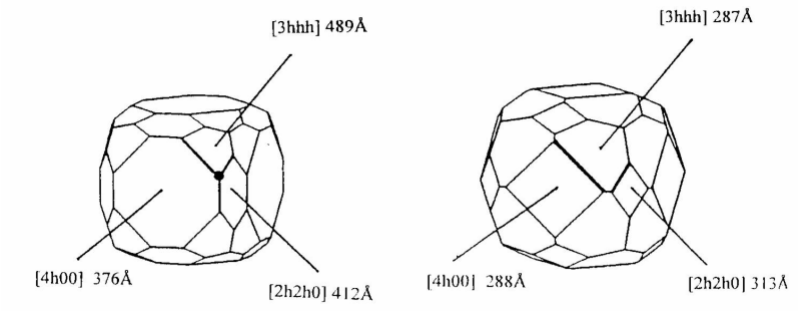


Fig. 4 (on the left)- It's a mobile device that can manoeuvre a spallation neutrons source, including a robot system that, moving on a controlled path, realize the conditions to observe emerging radiation of the sample, either movable or fixed in its place of normal exercise. It's a device with virtual goniometer. The neutrons diffraction requires the realization of conditions more binding respect other type of analysis and include the use of a system of convergent lens not basic in other type of application. (Patent in phase of PCT review).

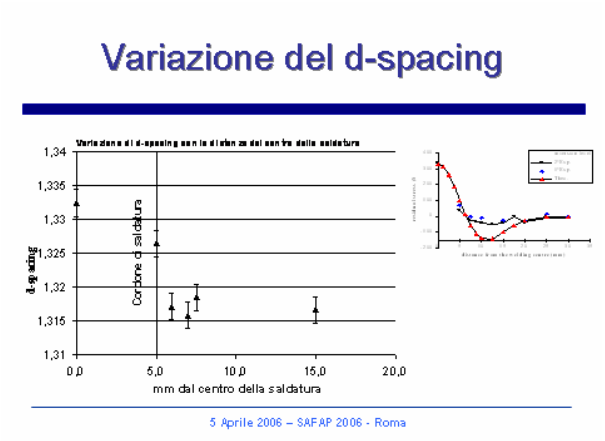
Fig. 5 (on the right)- Different analytical skill in function of the depth of surface shown by X ray and neutrons. Their resolving skill in function of direction and area of investigation not cover by ultrasound.





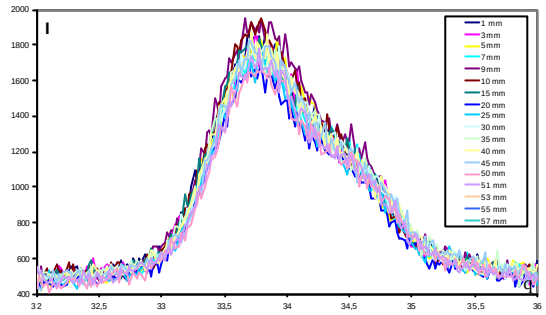
The potentiality of diffraction in the characterisation of materials are high and can even bring to determine the average volumes in terms of nm^3 of elements constituting the microstructure and the quality of lattices (i.e. the coherent domains). These are the characteristics that qualify the usability of a component and the material for the purpose assigned. It's clear that microstructures with spherical or cube-octahedral shape or with cylindrical shape can have differences in the preferential orientations. The usability and the qualification for such and the residual life of components may depend strictly on the presence of such preferred orientation in that they can be responsible for creep propagation and nucleation of cracks.

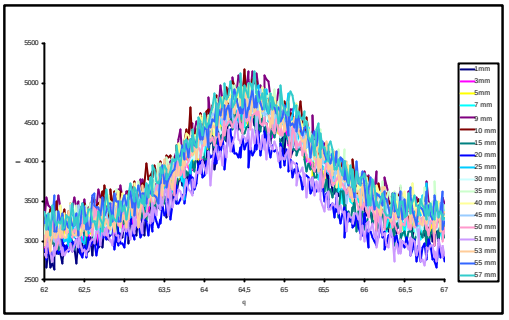
For investigation purposes via XRD or ND is not important working on types of components (i.e. vanes, tanks, plates or discs) but the type of material and the suitable wavelength (energy). The component is important, because its shape can make the reach of the point to investigate difficult. This problem can be limited by the mechanical and functional flexibility of the technology.



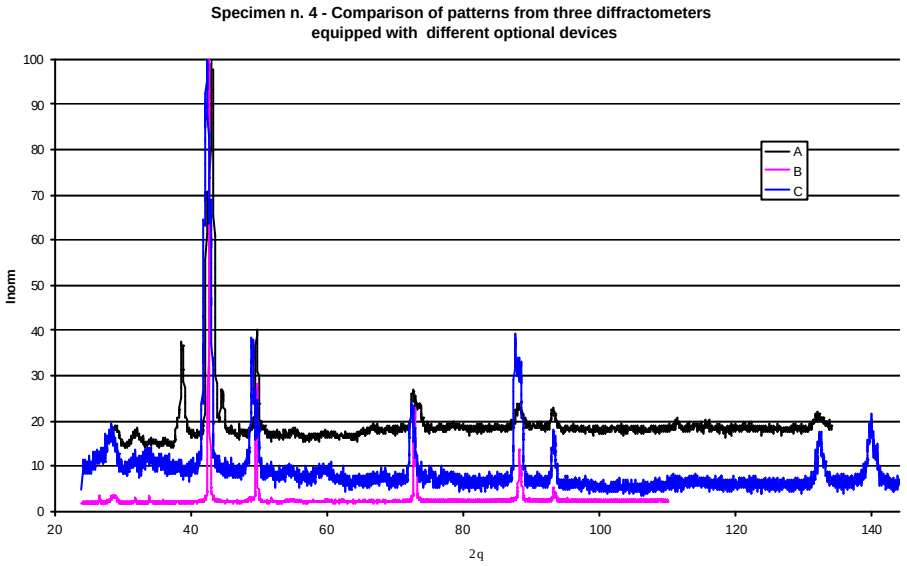
The figures show from the left to right: a. the analysis realised straddling a welding bead of a metallic foils, b. the instrument positioning and pointing for the measure, c. the trend of the d-spacing vs. the variation of the distance from the centre of the welding bead; in small figure the outlook of the residual stress trend.

The figure shows repeated XRD pattern obtained from a surface subjected to **shot-penning** at different distances from one side of the specimen.



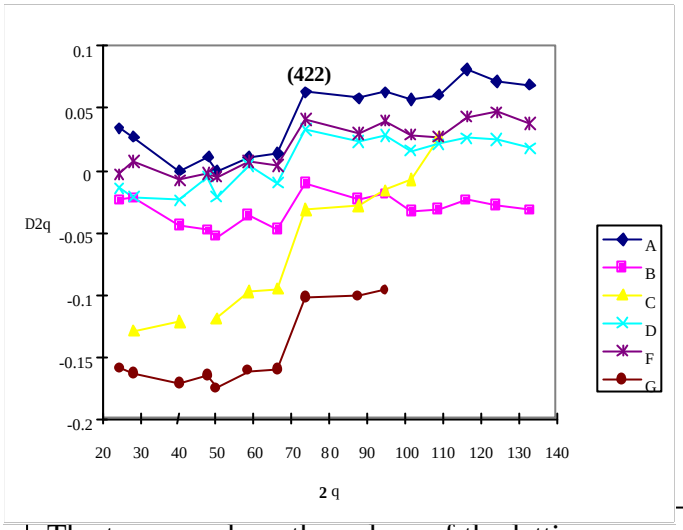


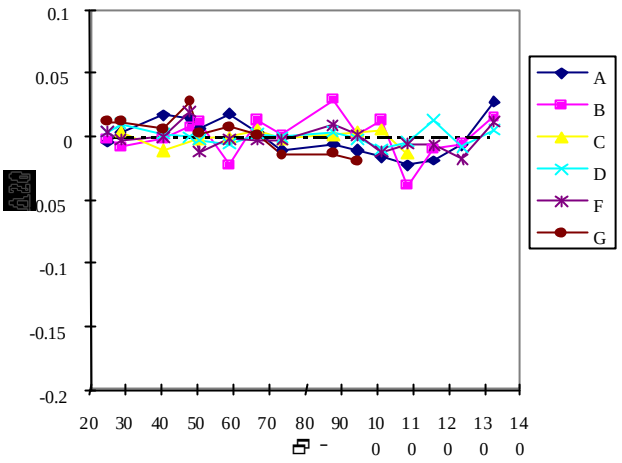
The analysis on metallic disckettes to be candidated as standard is reported below. The graphic shows a comparison of data collected from three different diffractometers on a same sample.



The graphic A comes from the diffractometer without x ray optics devices and in figure 2. It's possible to see some extra peaks produced by the non monochromatic radiation.
The graphic B is produced by a traditional diffractometer equipped with collimator and confinement slits (divergence, double Soller, receiving and a crystal monochromator curved on the diffracted beam).
The graphic C comes from a diffractometer equipped with nickel filter and polycapillaries semi-lens on the incident beam.
The huge difference of configuration among the various diffractometers is the cause of the evident difference in the data of the graphics. The graphics as are, have an apparently limited comparability. Certainly they cannot be compared "at eye" and at eye, the results obtained shall be considered not reliable. This unrealibility is apparent. In fact it depends on the difference on the measures processes.
The Methods developed in the 90's and defined "Diffraction Instrumental Monitoring" identifies the characteristic curve of the performance of diffractometers (just mentioned). The consideration of instrumental performances identifies the structural and instrumental characteristics of the material under exam with reliability (i.e. accuracy and precision) traceability according the field standards. The results of the following scheme should clarify the concept of reliability introduced by the use of Diffraction Instrumental Monitoring (DIM). (This results quoted in literature Berti, Powder Diffraction, 2001).

Dispersion of the peaks position **BEFORE** the use of DIM	Dispersion of the peaks position **AFTER** the use of DIM





The terms a_0 show the values of the lattice parameter BEFORE and AFTER the application of DIM. *Note: The uncertainty of the results reduce of a factor 100!*

Before DIM	**A**	**B**	**C**	**D**	**F**	**G**
a_o	6.2935	6.2898	6.288	6.2919	6.29251	6.255
Standard dev.	.0001	.0002	.002	.0001	.00004	.002
$Matrice_{var\text{-}covar}$	$.2\times10^{-7}$	$.6\times10^{-7}$	$.3\times10^{-5}$	$.1\times10^{-7}$	$.2\times10^{-8}$	$.5\times10^{-5}$
R	no	1	1	no	no	8
n° cycles	6	7	10	6	4	3
Observed peaks	15	15	10	15	15	10
Estimated h k l i	48	48	38	48	48	31
After DIM	**A**	**B**	**C**	**D**	**F**	**G**
a_o	6.2919	6.2917	6.2919	6.2920	6.2929	6.2919
Standard dev	.0	.0	.0	.0	.0	.0
$Matrice_{var\text{-}covar}$	$.4\times10^{-11}$	$.7\times10^{-11}$	$.3\times10^{-11}$	$.8\times10^{-11}$	$.4\times10^{-11}$	$.3\times10^{-12}$
R	no	no	no	no	no	1
n° cycles	3	3	3	3	3	3
Observed peaks	15	15	10	15	15	10
Estimated h k l i	48	48	38	48	48	31
Accuracy	$\pm1\times10^{-3}$	$\pm1\times10^{-3}$	$\pm10\times10^{-3}$	$\pm10\times10^{-3}$	$\pm2\times10^{-3}$	$\pm10\times10^{-3}$

The calibration protocol of the measure has to be experimented each time that there is an approach on a material that the device doesn't know.
This experimentation requires a variable time from three to six months for the XRD mobile.
A different approach of time and equipment is for the ND.

A brief resume of a work on a foil used as a screen. This work was presented in a national meeting.

XRD/XRF Non Destructive Testing on Alumina Refractory Brick

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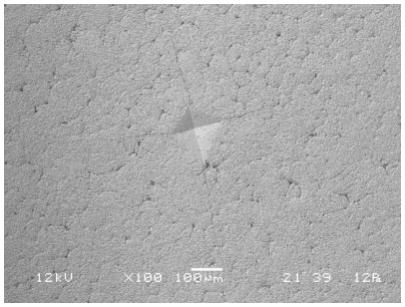
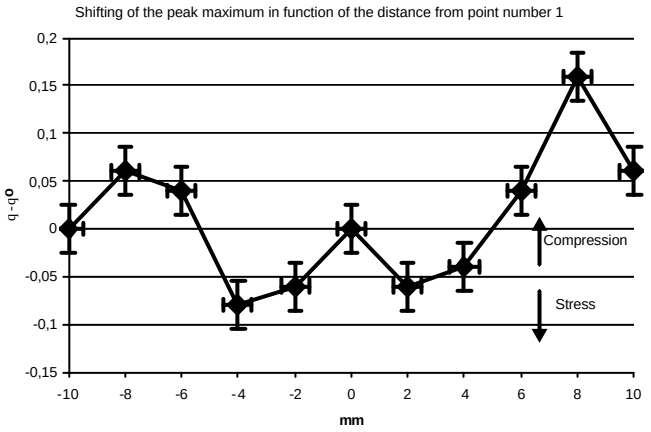
Alumina Refractory Bricks are widely used in a various industrial application as temperature resistant lining of ovens and furnaces, or external cover to protect components from suddenly and large temperature excursions. In many cases the presence of impurity and/or macrostress over a minimum acceptable amount is among the causes triggering faults and consequent dramatic damages. X-ray diffraction and X-ray fluorescence are in general good suited techniques to investigate the presence of elemental composition and the ordering quality of the elemental aggregation. These types of analyses are carried on using lab diffractometers and spectrometers on powdered specimens or on small plates; these specimens shall give the appropriate pattern to recover satisfactory information on the crystal chemistry composition. The influence of the instrument contribution is an equivalently well known problem for both types of analyses XRD and XRF. Here we are mainly focused on the capability of x-ray diffraction and fluorescence to provide satisfactory data collection from using movable equipments and using Non Destructive Testing (NDT) approach to the measurement. Analyses have been carried out on a composite material containing 99% of Alumina and other elements. A NDT-XRF data collection shows signals which are compatible with the presence in minor amount of several elements (i.e. calcium, barium, and others). The Figure on bottom left shows an example of Alumina refractory break where a shot has been intentionally induced. The objective of this work is to identify the presence of macrostrains and related effects on the diffraction pattern. The NDT-XRD analysis has been carried out on several points. These points were identified by a progressive number. The point labelled by 1 was loaded by an intentionally produced damage; the diffraction pattern shows a significant deviation from the position of the expected diffraction line as it is shown by Figure. The question is still open whether the presence of such impurity can be responsible for either magnify or reduce the deviation shown in Figure.





XRD analysis by movable diffractometer (DifRob®)