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Asymmetric nanocomposite cellulose acetate/silver ultrafiltration membranes - Permeation performance and antibacterial effect
Supervisors: Maria Norberta Neves Correia de Pinho / Luís Miguel Minhalma
Abstract: Asymmetric cellulose acetate/silver nanocomposite membranes were prepared by dispersing silver nanoparticles in the cellulose acetate casting solution with different solvent ratios (acetone and formamide) to produce membranes with a wide range of pore sizes. Silver nanoparticles were synthesized ex situ and added to the casting solution. The nanocomposite membranes prepared resulted in a continuous film without pinholes with yellow to brown color indicating the presence of silver nanoparticles; hydraulic permeability and molecular weight cut-off of the nanocomposite membranes increased when compared with the cellulose acetate membranes; silver nanoparticles are retained in the membrane structure and the nanocomposite membranes presents a growth inhibition of bacteria in water and a decrease in the number of colonies over time in a E. coli suspension that is in contact with nanocomposite membranes.

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Design, construction, characterization and bilateral comparison of an air-kerma cavity standard
Supervisors: Lídia Ferreira
Abstract: Ionizing radiation is a fundamental tool in contemporary medicine. The radiation protection of patients is a major metrological concern, since the delivered dose is the last step of a complex dosimetric process, starting in the primary standard definition. This thesis represents the first effort in Portugal for the construction of home-made standards, and describes all the steps in the development of a graphite cavity chamber for the measurement of air-kerma in the energy range of $^{60}$Co. The work is consonance with the European pursuit of a more accurate metrological basis for quantities related to the safe use of ionizing radiation.

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Laser Ablation of Dentin and its Medical Application
Supervisor: Rui Vilar
Abstract: The present work aims at studying the femtosecond laser ablation of dental hard tissues for application in dental treatments. The surface morphology, structure and chemical constitution of the laser treated surfaces were investigated to obtain information about the laser-material interaction. The clinical performance of laser treated dentin surfaces was evaluated by mechanical shearing tests to measure the adhesion to dental adhesive and by measuring the temperature increase in the pulpal chamber of the tooth due to laser treatment. The results showed that the ablation of enamel was accompanied by melting, even for fluences just above the tissues' ablation threshold. Laser treated dentin surfaces presented no sign of resolidified material and the tissues' chemical constitution was preserved. Enamel ablation occurs mainly by photothermal mechanisms involving rapid heating to high temperatures followed by ablation by liquid spallation or phase explosion. The ablation of dentin is influenced by the ablation of heat sensitive collagen fibrils, which provide the cohesive strength of the tissue, leading to tissue removal by a photomechanical mechanism (solid spallation). Due to the lack of thermal damage to the laser treated dentin surfaces, the dental adhesive could infiltrate into the tissue even without acid etching, establishing good adhesion with the tissue. The shear strengths of the laser treated material were comparable to the values obtained for conventional drilling. However, heating of the tissues was unavoidable, especially with high laser fluences, high pulse repetition rates and long treatments. Therefore, external cooling during the laser treatment is recommended.
Ultrafast Laser Tissue Cutting and Removal for Applications in Orthopaedic Surgery
Supervisor: Rui Vilar / Victor Oliveira
Abstract: The main objectives of this thesis are to evaluate ultrafast lasers as cutting tools for orthopaedic surgery and to find operating conditions that minimise bone degradation. Bovine cortical bone samples were treated using two lasers, a Yb:KYW laser (1030 nm) and a Ti:Sapphire laser (775 nm). The ablation thresholds were determined, and a wide range of processing parameters was tested in order to evaluate their influence on the ablation surfaces. Two refrigeration methods were tested, water irrigation and helium gas atmosphere, to prevent major thermal effects. Determined ablation threshold fluences are 0.79 and 0.73 J/cm² for 130 and 560 fs Yb:KYW laser pulses, respectively, and 0.63 and 0.93 J/cm² for 25 and 100 fs Ti:Sapphire laser pulses, respectively. The surfaces treated with fluences below 2 J/cm² and pulse frequencies below 1 kHz are relatively well preserved, with the amount of collagen diminished only at the first tens of nanometres at the surface, and the hydroxyapatite structure intact. For fluences between 2-16 J/cm², the organic compounds are completely removed and the hydroxyapatite in bone decomposes; the extent of these thermal effects increases with the fluence. A theoretical approach allowed deducing that the predominant ablation mechanism taking place at lower laser fluences is liquid spallation, while the surfaces treated with higher fluences suffer phase explosion. The unwanted damage can be almost totally avoided if water irrigation is used, but not as much if helium gas is used. Finally, we were able to produce LIPSS (laser-induced periodic surface structures) on cortical bone surface which is unprecedented in biological hard tissues.

Neutron dosimetry and spectrometry studies for radiological protection using the nTOF spectrometer at CERN
Supervisors: Lidia Ferreira

Masters Dissertations

Efeitos de escala na resistência mecânica de materiais
Supervisors: P. Rosa / A.C. Ferro
Abstract: The consumer market has stimulated the miniaturization of technological equipment. This demand becomes it necessary to rethink the manufacturing processes in the light of the scale effects. Among the manufacturing technology, plastic deformation processes have particular relevance. This research seeks to analyze the existence of scale effects on the mechanical strength of commercial purity aluminum alloys in quasi-static conditions. The scale effect is introduced with the regulation of the metallurgical grain size. Comparison of different stress-strain curves at uniaxial compression tests has shown the existence of scale effects. This result allowed the establishment of a hard-plastic constitutive model.

Growth and characterization of low dimensional Mo selenides
Supervisor: Olinda Conde
Abstract: Mono- to few-layer MoSe₂ nanofilms were synthesised onto SiOₓ/Si substrates by Chemical Vapor Deposition (CVD), using MoO₃ and Se powders as solid precursors. The experiments were carried out at atmospheric pressure, using Ar as the carrier gas and H₂ as the reducing agent. The deposition parameters were tuned to understand their influence on the morphology, crystallinity and number of layers of the deposited material. The results indicate that the growth of mono- and bi-layer MoSe₂ triangle flakes strongly depends on the concentration of H₂ in the gas phase, the Mo:Se ratio at the substrate surface, the gas flow rate and the uniformity of the deposition temperature along the substrate length.
Influence of laser-induced surface nanotextures on the tribological behaviour of silicon
Supervisor: Rui Vilar
Abstract: LIPSS (laser-induced periodic surface structures) are nano-sized periodic surface
features and have been intensively investigated because a general theory for their formation
is still missing and because they have a profound effect on the materials surface properties,
potentially leading to interesting applications. In the present work the effect of LIPSS on the
friction of silicon sliding in dry conditions was investigated. The friction properties of silicon
samples polished and surface treated were compared using a ball-on-at nanotribometer. In general,
LIPSS do not decrease the friction coefficient in comparison to the polished material but material
transfer seems to be reduced.

Estudo do efeito anti tumoral e antioxidante de diferentes frações recuperadas do efluente da
cortiça através do processo de membranas
Supervisors: Luís Miguel Minhalma / Rita Isabel Dias Pacheco
Abstract: In this work, the assessment of the biological activity and identification of valuable
polyphenols compounds in cork processing wastewater was envisaged. These compounds were
obtained using two cellulose acetate (CA) ultrafiltration (UF) membranes, with MWCO of 3
kDa and 74 kDa. The fractionation and purification of the polyphenols were made recurring
to permeation experiments running in concentration and diafiltration modes. The wastewater
and the fractions were tested for antioxidant and anticancer activity, showing high antioxidant
activity and revealing not to be toxic against carcinoma breast cancer cell lines MCF-7, but
efficient as inhibitors of cell proliferation.

Bactericidal effect of silver in cellulose acetate mixed matrix membranes: Silver nanoparticles vs
silver loaded zeolite
Supervisors: M. A. Lemos / M. N. Pinho
Abstract: Nanofiltration is still affected by biofouling, which can be minimized using mixed
matrix membranes with antibacterial properties. Thus, seven cellulose acetate asymmetric
composite membranes were prepared via the wet-phase inversion method incorporating, in the
membrane casting solutions, silver nanoparticles, ZSM-5 zeolite and different contents of silver
exchanged zeolite (0.005%, 0.03%, 0.07% and 0.14% of silver in the membrane). The silver
zeolite membrane (0.14% silver) showed the lowest bacterial growth of *Escherichia coli* and
*Pseudomonas aeruginosa* after 300 minutes. The zeolite had no bactericidal effect against the
cultures, contrary to the silver exchanged zeolite that showed higher effect against *E. coli*. 
Ultrafiltration and nanofiltration of E-stage bleaching plant effluent of a sulphite pulp mill
Supervisors: Ann-Sofi Jonsson / M. N. Pinho
Abstract: With the continuous increase of the environmental constraints in the pulp and paper industry, efforts have been made to find possible ways that minimize water consumption by reusing treated process streams and improving the quality of the final effluent. In addition, the use of by-products from this industry increase its economic sustainability. The treatment of sectorial streams in the pulp mills can be an attractive alternative due to its lower volumes and more specific characterizations in comparison to the final effluents. Thus, the aim of my work was to evaluate the use of a membrane separation process in the treatment of a bleaching plant effluent.

NMR study of the twist-bend nematic phase
Supervisors: João Luis Maia Figueirinhas / Carlos Manuel dos Santos Rodrigues da Cruz
Abstract: In this work, we attempted to characterize the molecular orientational order in the CBC9CB dimer system in both the uniaxial and the twist-bend nematic phases, using proton and deuterium NMR spectroscopy. We concluded that, starting at the N_{U}-N_{TB} phase transition and increasing in the N_{TB} phase, the change in the orientation of the most ordered molecular axis, leaving the symmetry plane defined by the carbon-deuterium bonds in the chain positions adjacent to the aromatic rings, along with the verification that the molecular biaxiality assumes a non null value in the N_{TB} phase are the main factors that account for the change in the molecular orientational order observed in the system.

NMR study of the molecular dynamics in magnetic and non-magnetic ionic liquids
Supervisor: Pedro Sebastião
Abstract: In this work, NMR (relaxometry, spectroscopy and diffusometry) and viscometry experiments were carried out in order to understand the molecular dynamics and self-diffusion behavior of magnetic and non-magnetic ionic liquids (ILs)-based systems. Aliquat-iron-based magnetic and non-magnetic ionic liquids comprising different concentrations (1% and 10% (v/v)) of DMSO were studied. The results suggest that, when at low concentrations, DMSO produces an increase of the superparamagnetic effect and promotes a more structured ionic display. A set of magnetic ionic liquids (MILs) based on a phosphonium cation ([P66614]) and on a gadolin-ium anionic structure were also analyzed in order to evaluate and characterize the superparamagnetic effect produced by this magnetic complex in comparison with the reported iron-based anionic structures. Mixtures comprising different concentrations of MIL were studied and a saturation effect, which leads to a decrease in the superparamagnetic properties with the increase of the concentration of magnetic particles, was detected.
Abstract: The main objectives of this thesis were to investigate the surface texturing of a Pd-based bulk metallic glass (BMG) using a femtosecond laser direct writing method, as a potential technique to modify the surface topography and properties of the material. A laser Yb:KYW laser (1030 nm) was used. The evolution of the surface textures with the radiation fluence and number of laser pulses were studied, the damage thresholds determined and the surface textures formation mechanism discussed. A preliminary evaluation of the tribological behaviour of the laser texture Pd-based specimen in dry conditions was performed using a nanotribometer. The treated surfaces were characterized by SEM, EDS and XRD. The damage threshold fluence for the Pd-based BMG was 0.09 J/cm² for 50 Yb:KYW laser pulses. The chemical composition and the amorphous structure were not modified after the surface laser treatment. Four different surface textures were identified, which were characterized by 3D surface reconstruction based on stereoscopic pairs. T0 forms for lower fluences and it can be identified as High Spatial Frequency Lipss (HSFLs) with a periodicity of 470 nm, with a formation mechanism described by Sipe's theory. The T1 morphology forms for higher fluences. It presents a directionality that is due to the incubation of liquid around surface defects. At higher average fluences T2 and T3 form due to hydrodynamic instabilities. The temperature gradients and the energy absorption control the formation of the instabilities, leading to the formation of texture T2, perpendicular to the laser beam polarization. T3 is the final stage of the hydrodynamic instabilities, where the liquid film starts to breakdown into lumps, as a result of a spinodal dewetting mechanism.

Caracterização de propriedades termo-electricas de metal duro

Supervisors: A. Almeida / R. Vilar

Abstract: This work aims to study the thermal properties of several WC-Co formulations with average size of WC particles between 0.8 and 8 µm and Co content between 3.5 and 25%, produced by pressing and sintering. The microstructure consists of faceted angular particles of α-WC dispersed in a matrix of α-Co which volume fraction varies between 4 and 34%. The hardness increases with decreasing average grain size and decreasing Co content. The influence of Co content is more significant and is due to the decreasing fraction of the hard phase in the constitution of the material. The hardness varies from 883 HV1 for a sample with 4 µm grain size and 25% Co to 2128 HV1 for the 0.8 µm grain size and 3.5% Co material. The thermal diffusivity was determined by the laser flash method, between 150 and 800°C, and the electrical resistivity was determined at room temperature by the four-point technique. Both the thermal diffusivity (thermal conductivity) and electrical conductivity increase with the average grain size due to the decrease of the total area of grain boundaries which are regions of high defect concentration, causing dispersion of the electrons. The effect of the Co content in thermal and electrical conductivity is less clear. An increase in thermal and electrical conductivity with the Co content is observed in fine grain samples containing up to 6% Co, then in the range from 6 to 20% Co content seems to have no effect and for higher contents of Co an increase in these properties is observed. This last trend may be explained by the presence of W and C in solution in Co, however, the behaviour observed for lower Co contents remains unexplained and requires further study.

Comportamento Tribológico de Superfícies Metálicas Nanotexturadas com Lasers de Femtosegundo

Supervisor: Rui Vilar / A. Almeida

Abstract: MEMS (Microelectromechanical Systems) are devices with very small dimensions, typically ranging from 100 to 1 mm. This causes high adhesion and friction forces in these mechanisms' surfaces, reducing their wear resistance and eventually causing their catastrophic failure. In this work we tried to reduce the friction and wear between the surfaces of a tool-steel, through surface laser texturing by femtosecond laser with LIPSS (Laser Induced Periodic Surface Structures) and lubrication with MoS2. Tribological tests were carried under the ball on plate configuration, using linearly reciprocal sliding and rotation conditions. The tests allowed measuring the friction and wear coefficients of the different surfaces: polished and laser-textured, with and without lubricant. In the laser-textured samples, the wear tests were made under the perpendicular and parallel sliding directions to the LIPSS. The worn surfaces were analysed by scanning electron microscopy. In the LIPSS covered surfaces the friction and wear coefficients are lower than those of the smooth surface, the lowest values being observed in the perpendicular sliding direction. In this sliding direction LIPSS resist wear for longer times. Even lower friction and wear coefficients were observed in the lubricated laser-textured samples, and the sliding direction was shown to be indifferent. The analysis of the worn areas indicated that delamination wear had occurred in the dry surfaces, with the formation of a tribolayer consisting of oxide particles.
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Dilute magnetism in graphene
Supervisor: Eduardo Castro

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Carrier transport and energy harvesting in ZnO nanowires
Supervisor: R. Schwarz

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pMOSFET fabrication using a low temperature pre-deposition technique
Supervisors: Guilherme A. R. Lavareda / Carlos A. N. Carvalho

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Membranas de matriz mista
Supervisors: M. C. Gonçalves / M. N. Pinho

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Development and modelling of mechanical alloying for production of copper matrix composite powders reinforced with alumina and graphite
Supervisor: A. C. Ferro