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Fretting fatigue life prediction for state-of-the-art materials and structures

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Life of structural elements subject to fretting fatigue, tribofatigue and contact fatigue is predicted with innovative techniques developed by the author, colleagues from the Tribofatica Scientific Association (Belarus), and researchers of Western schools of fretting fatigue (Germany and Spain).

Fretting fatigue occurs at relative displacement (slip) of a cyclically loaded structural component and a clamped counterbody. Normal and shear surface stresses in slip give rise to early nucleation and quick propagation of short cracks with the stress intensity factors (SIF), being inversely proportional to the crack length, while SIF of normal is directly proportional to it. Fracture mechanics approach is widely used for prediction of fretting fatigue propagation phase, corresponding to the larger share of the structural component total life.

Mode (KI and KII) initial crack propagation, dependent on the friction coefficient, is controlled by different criteria, viz. the maximum tangential stress criteria by Otsuka, maximum normal stress criterion, etc. For structural components/counterbodies of different geometries, the combination of surface and bulk stresses controls the crack propagation direction and its rate, inducing recurrent variation of the total stress ratio R . This variation is accounted for via the Elber-Marci Keff concept modified by the author, while the effect of negative residual stresses, induced by shot- and laser peening, on SIF and total life is simulated.

Fretting fatigue life calculation results are presented for specimens and structural components from state-of-the-art aluminum and titanium alloys. Analysis of advanced fretting fatigue research outcomes confirms that this factor becomes critical for the in-service endurance of modern materials, and the fracture mechanics and tribological measurement-based calculation techniques provide a robust fretting fatigue life prediction, which may be extended to other domains of rigid body mechanics.

Thermodynamics Assessment of Extra Mn Addition in the Recycling of a LM24 (Al-Si-Cu) Aluminium Alloy

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Abstract. Iron contamination from scrapped materials is always a problem in producing high quality secondary aluminium alloys. Consequently, the iron removal during recycling of aluminium alloys is essential and important in industrial practice. This work aims to study the effect of extra Mn addition on the effectiveness and efficiency of iron removal during recycling. The thermodynamics assessment was carried out for a LM24 (Al-Si-Cu) alloy to find out the variation of balanced iron and manganese in the liquid melt and in the sediment solid Fe-rich intermetallics with different levels of extra Mn addition. The effect of alloy composition and processing temperatures was investigated. The findings help to understand the capability and fundamentals of iron removal in aluminium alloys.

Keywords: Aluminium alloys, thermodynamics, phase formation, materials recycling, iron removal

Acknowledgement

The financial support from EPSRC and TSB (UK) is gratefully acknowledged. Dr. Feng Gao and Dr. Wenchao Yang at BCAST, Brunel University, took part in the project.

Miniature sources of irradiation for intracavitary thermo radiotherapy

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Abstract. This report presents the development of a miniature ionizing and thermal radiation source for oncological diseases treatment namely the inward parts of the body. This source can be placed next to the tumor inside of the body. This report is only about methods and devices for the intracavitary therapy. Irradiation by external sources wasn't considered in our investigation.

Keywords: X-ray Therapy, Thermo Radiotherapy, Intracavitary Therapy, Miniature X-ray Source, Nanocomposite Tungsten, Carbon Nanotubes.

Magnesium Based Nanocomposites: Light Weight Materials of the Future

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Magnesium (with density, $\rho = 1.74 \text{ g/cc}$) being $\sim 35\%$ lighter than aluminum and $\sim 70\%$ lighter than steel is an attractive and a viable candidate for the fabrication of lightweight structures. Progressive research advancements have been made so far to utilize the magnesium (Mg) based materials in various technology-driven applications. Recently, the incorporation of inexpensive nanoscale ceramic particles to Mg has received astounding attention, as it promises a new class of Mg materials called Mg-metal matrix nanocomposites (Mg-MMNCs) which displays superior strength and/or ductility, corrosion resistance, high temperature properties and wear resistance without noticeable weight gains. In this talk, an overview of the processing and properties of various Mg-MMNCs will be presented. First, the innovative and cost effective processing methodologies such as disintegrated melt deposition method and microwave assisted bidirectional rapid sintering technique will be briefly introduced. Later, the mechanical and corrosion characteristics of various Mg-nanocomposite formulations produced using the above mentioned methods will be presented. Finally, an account of on-going research initiatives in the development of novel light weight Mg nanocomposites will be highlighted.

Chemical Reactions in the Alumina-Carbon/Iron system at 1550°C

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We report wettability investigations on Al_2O_3 -C (10-90% C) substrates with molten iron at 1550 °C in argon atmosphere for time periods up to 6 hours. The presence of molten iron was seen to act both as a reducing agent and a metallic solvent. For carbon content in the substrate ranging between 10-40%, the video images of the iron droplet started to show minor deviations after 30 minutes of contact followed by intense activity in the form of fine aluminium oxide whiskers emanating from the droplet and on the refractory substrate. The interfacial region also changed significantly over time and the formation of small quantities of iron aluminide intermetallics was recorded after 30 minutes as a reaction product in the interfacial region. These chemical reactions also caused extensive penetration of molten iron into the refractory substrate. This finding could have significant implications for refractory degradation and contamination of steel with reaction products.

The in-situ synchrotron X-ray diffraction investigation of the deformation-induced martensitic transformation of the metastable austenite in Fe-13%Cr-4%Ni stainless steel

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Abstract: In order to reveal the mechanical stability of the metastable austenite during the tension loading in the Fe-13%Cr-5%Ni martensitic stainless steel, a mini tensile instrument has been designed and installed on Shanghai Synchrotron Radiation Facility to conduct the in-situ synchrotron high energy X-ray diffraction (SHXRD) experiment during the uniaxial tension. The quantitative phase fraction calculation indicates that the metastable austenite in the 620°C*5h tempered sample transforms to martensite occurring at the elastic stage and through the whole deformation. The intrinsic yield strengths and mechanical behaviors of the metastable austenite and martensite during deformation have been analyzed by FWHM and lattice strain. It has been found that the micro-yielding of metastable austenite and martensite promote the development of the deformation-induced phase transformation. The deformation-induced transformation related to the mechanical stability of metastable austenite is analysis by the local carbon concentration and the distribution location of austenite.

Key words: Metastable austenite; Martensitic stainless steel; Synchrotron high-energy X-ray diffraction; Micro-Yielding; Deformation-induced phase transformation

Abrasive Wear of Oxide and Non-oxide Ceramic Phases

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Abstract. The application of structural ceramics is at present a common trend in machines and construction of mechanical devices. Dense ceramic sinters made of alumina, zirconia, silicon carbide or silicon nitride replace very often metallic parts. The advantages of ceramics are especially evident when they work as parts of machinery exposed to the action of loose and hard particles. The paper compares the abrasive wear susceptibility of commonly used, relatively inexpensive ceramic sinters made of alumina and alumina/zirconia composites to the wear of much more expensive in fabrication non-oxide sinters. Silicon carbide, silicon nitride and two non-oxide composites were selected as examples of extremely wear resistant materials. Two types of tests were performed. Dry Sand Test, which indicates wear susceptibility of the material to the wear during the abrasive action of hard particles without any lubricant, was the first one. Miller Test was the second. This test examined the wear of materials during the action of hard particles in wet environment (pulp). In both tests the same abrasive silicon carbide powder was used.

The level of densification of the investigated materials was performed. The internal stress state caused by thermal expansion coefficients of constituent phases mismatch was estimated according to the theoretical model. The test results proved that the influence of the second phase presence in the materials was distinct for the wear rate in both applied work environments.

Keywords: Abrasive Wear; Alumina; Silicon Carbide; Silicon Nitride; Dry Sand Test; Miller Test

Structural and functional properties of (Cu, N) co-doped ZnO films

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Highly transparent and conductive (Cu, N):ZnO thin films with application in transparent electronics were obtained by sol-gel spin coating deposition. The effect of N doping and (Cu,N) codoping on their structure, optical and conductivity properties were analyzed by electronic microscopies, XRD, PL, optical transmission/absorption and electrical measurements. SEM, TEM and XRD data evidenced that (Cu, N) codoping determines a decrease of crystallinity, as well as of the films porosity. The dislocation density increases from $1.22 \times 10^{-3} \text{ nm}^{-2}$ in N: ZnO to $13.64 \times 10^{-3} \text{ nm}^{-2}$ in (Cu, N):ZnO films and the residual stress from 6.57 to 8.77 GPa. The near UV PL emission band shifts to red spectral region in codoped films. The absorption edge is sharp, which demonstrates the low porosity of these films. The transmission increases from 92 % in N:ZnO to 94 % in (N, Cu): ZnO. The codoped films exhibit photogenerated currents under UV light irradiation. The electronic structure of the doped and codoped systems is investigated also by abinitio calculations.

Influence of Zr addition on the phase decomposition of Al-6Mg-0.4Sc studied by positron annihilation spectroscopy

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Abstract: In this work, the results of positron annihilation spectroscopic studies of the precipitation behaviour in 0.2 wt.% Zr-doped Al-6Mg-0.4Sc alloy under different isothermal annealing conditions are reported. In an earlier investigation on the base alloy Al-6Mg, the modifications in the precipitation kinetics as a result of inclusion of 0.4 wt.% Sc had been monitored and the precipitates of Al₃Sc had been identified as the main positron trapping sites. Although Sc has better diffusivity in Al-6Mg than Zr, the latter appeared to be an ideal additive to generate new species of precipitates of the stoichiometry Al₃Sc_{1-x}Zr_x and the differences had been reflected in the positron lifetimes as well as in the coincidence Doppler broadened ratio curves. It is postulated that Zr forms complexes with vacancies. Annealing at higher temperature resulted in the dissociation of complexes and precipitation of Al₃Sc_{1-x}Zr_x. As the extent of annealing increased, x increased to attain a definite stoichiometry for the precipitates. Further increase in annealing temperature led to the segregation of excess Zr atoms on the surfaces of the precipitates. Transmission electron microscopy showed a spheroidal precipitate with complete absence of facets. It implied the segregation of atoms to modify the surface morphology of the precipitates.

Keywords : aluminium alloys, defects, phase decomposition, positron annihilation, precipitation, scandium, zirconium doping

High temperature phase transformation of designed ternary Ti-Al-Nb alloys for directional solidification

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In this study, phase transformation phenomenon at high temperature was investigated by using designed Ti-Al-Nb alloys with addition of 3rd element (β stabilizer). 40mm long sample was obtained by directional solidification method at 1600°C in Bridgman type furnace with 45 and 90 mm/h growth rate in argon atmosphere, and then followed quenching. Solidification microstructure of primary phase at solid/liquid interface in quenched specimen was analyzed. Thermal analysis of transformation temperature was investigated at temperature range from 900°C to 1600°C with increasing rate 4°C/min. As a result, volume fraction of primary α and primary β phases at liquid/solid interface in coincident with growth rate and composition were observed at dendrite arm areas. It was also revealed that the estimated melting temperature and the phase transformation temperature of designed alloys were almost same as that we estimated through the thermal analysis.

*This Following are results of a study on the “Leaders in Industry-university Cooperation (LINC)” Project, supported by the Ministry of Education and the National Research Foundation of Korea (NRF).

Keyword: Directional solidification, stabilizing element, High temperature transformation, Ti-Al-Nb alloy, Intermetallic compound.

A bonding study of TiAl and SCM440 by friction welding

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In this study, the microstructure and related mechanical properties of friction welded TiAl (superior characteristic high temperature & specific strength) and SCM440 (alloy steel for machine structural use) were investigated. The friction welding was performed using a servo-motor type friction welding machine for control the several variables. Experimental variables were changed in order to bond the test pieces between TiAl to TiAl, SCM440 to SCM440 and TiAl to SCM440. Scanning electron microscopy (SEM) was used to observe microstructural evolution taking place during friction welding. Universal testing machine (UTM) was used for tensile test to reveal whether the fracture occurred in base metal zone or welding zone. It was found that several variable (up-set, up-set time, rpm, force, etc) changes could be caused in different heat-affected zone size, welding bead shape, microstructure and resulted in hardness changes in welded zone. Through observing the bead shape of weld by friction welding, we can confirm melting temperature of metal is important at friction welding test of similar and dissimilar metal. Because of formation of bead of weld was depends on metal of melting temperature. Therefore If do not reach to metal's melting temperature, bead of weld can be deformed only on side. We applied taper on cross section of metal, It will be influenced on weldability due to reduced blurring. Therefore machined taper shaped on cross section can improve the mechanical properties and weldability.

*This Following are results of a study on the “Leaders in Industry-university Cooperation (LINC)” Project, supported by the Ministry of Education and the National Research Foundation of Korea (NRF).

Keyword : TiAl, SCM440, Friction Welding, Servo-motor, Dissimilar metallic bonding.

Roughness measurements of deep drawn 3003 aluminum alloy after surface treatment

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The purpose of this study was resolution of the state for losing of metallic luster and boundary occurring phenomenon on the surface of 3003 Al alloy after deep drawing. When deep-drawing was performed, scuffing by frictional force was the reason for losing of metallic luster and boundary, results in ununiformed surface. These defective product was retreat by one of the methods such as mechanical polishing, chemical polishing, and electrolytic polishing. In this study, a buffing was introduced as a mechanical polishing,, chemical polishing such as Alupol(2) and Alcoa were also performed, and electrolytic polishing method was performed by using general electrolyte and phosphoric acid. The microstructure observation was performed by Optical Microscope (OM) and Atomic force microscope (AFM), and texture measurement was performed by using XRD. It was found that overall roughness was found to improve with proportion to time. It was also found that the mechanical polishing method was expected to improve the loss of metallic luster on short time. Chemical polishing method was expected not only to improve surface roughness but also corrosion resistance by oxide film forming. Electrolytic polishing method was expected to improve surface roughness to lowest level. Therefore, it could be suggested that proper surface roughness could be achieved by one of the subsequent operation.

*This Following are results of a study on the “Leaders in Industry-university Cooperation (LINC)” Project, supported by the Ministry of Education and the National Research Foundation of Korea (NRF)

Keyword: 3003 Aluminum alloy, deep drawing, buffing, chemical polishing, electrolytic polishing, surface roughness

Paper Title: Investigation of basic thermodynamical and transport data of binary systems of polyethylene glycol (PEG)/CO₂

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Knowledge of basic thermodynamic and transport data is of fundamental importance for process design in order to satisfy economical requirements. Behaviour of polyethylene glycols with different molar masses (ranging from 1,000 g/mol do 100,000 g/mol), solubility and diffusivity in the binary systems with CO₂, as well as the volume variation of the polymers were analysed in the first step with two different methods; a simple gravimetric method developed by the authors and a method using Magnetic Suspension Balance at same process conditions (in the pressure range from 10.0 MPa up to 40.0 MPa and a temperature of 343 K). Results obtained by both methods were compared in order to validate the results.

Capillary rise method adapted to the measurement conditions and sample properties was applied to investigate the interfacial tension. Obtained results were in a good agreement with the literature data since the discrepancy was lower than 2.4 %.

Keywords: polyethylene glycol, CO₂, diffusivity, solubility, density, interfacial tension (IFT); capillary Rise (CR) method.

Microstructural design of new high conductivity – high strength Cu-based alloy

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Copper-based high strength conductive alloys are used in a myriad of applications in automotive, aeronautic and electronic industries. The demand of these materials is booming. The strongest conductive alloy is based on the Cu-Be system which has the disadvantage of toxicity and cost. There is a great demand for the replacement of Cu-Be alloys by new toxic free and environmentally friendly high strength-high conductivity materials. In an attempt to find an alternative, we focused on the Cu-Mg system. We have designed in that system some novel high conductivity-high strength materials. They exhibit an excellent balance between strength and electrical properties. The properties and the performance of the designed materials are compared with the main Cu-based alloys and the analysis shows that they perform equally to the best one (Cu-Be). Furthermore, we show that an increase of Mg content modifies the microstructure feature and leads to a strong increase of strength without any significant deterioration of the electrical conductivity. This behavior was attributed to the formation of eutectic islands in which high density of Cu₂Mg nanoparticles precipitate.

Design and optimization of an ultrasonic spray pyrolysis system for production of titanium dioxide nano-structures for solar cell electrodes

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Abstract. Ultrasonic Spray pyrolysis (USP) provides a cheap, fast and reliable way or means of depositing various materials as thin films, nano-particles and nano-structures. The need for precise control of properties has sparked researches on aerosol processes that may replace conventional expensive and complicated solid state techniques for production of titanium dioxide nano-powders. Based on experiences gained, whilst working with USP for production of nano-powders a novel USP system was designed and constructed. This system was optimized for the production of thin films and nano-structures of titanium dioxide for solar cell applications. The paper starts off with an overview of TiO₂ deposition methods. Then it presents the various considerations that were used during the design and construction phase.

Key Words: Ultrasonic spray pyrolysis, TiO₂, nano-powders, Solar cell

Rheological Properties of Thermoplasticpolyurethanes

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ABSTRACT. The effects of the molecular aggregation structure on the rheological properties of thermoplastic polyurethane (TPU) were investigated. The TPU was composed of poly {(tetramethylene adipate)-co-(hexamethylene adipate)} glycol as the soft segments, 4, 4'-diphenylmethane diisocyanate and 1,4-butanediol as the hard segments. The TPU sheets prepared by injection molding were annealed at various temperatures from 23 to 120 °C to vary the molecular aggregation structure. Glass transition temperature of the soft segment and melting points of the hard segment domains of the TPUs decreased and increased, respectively, with increasing annealing temperature. The results of DSC, solid-state NMR spectroscopy and dynamic viscoelastic measurements revealed that the degree of microphase separation of the TPUs becomes stronger with increasing annealing temperature due to the progress of formation of well-organized hard segment domains. The dynamic temperature sweep experiments for molten TPUs revealed that the temperature at critical gel point, which is defined as the temperature at which the dynamic storage modulus coincides with the loss storage modulus, in the cooling process increased with the progress of aggregation of the hard segments in the TPUs observed in the solid state. The uniaxial elongational viscosity measurements showed that TPUs exhibited an obvious strain hardening behavior with strain rate owing to residual hard segment domains at an operating temperature. It was revealed that the formation of well-organized hard segment domains had a profound effect on the rheological properties of TPUs, in particular on their elongational viscosity.

Keywords: Molecular aggregation structure, thermoplastic polyurethanes, rheological properties, annealing, solid-state NMR, critical gel point, uniaxial elongational viscosity, strain hardening.

Sol Gel technology: A key tool to develop nanomaterials for material and environmental applications

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Abstract. The sol-gel process is one of the fascinating techniques to develop inorganic nano-fillers that can be further used for developing nanocomposites for various applications. In our research activities, we have used these sol gel technique to derive organic-inorganic hybrids using carbon producing material such as lignin and 1,3 propane diamine etc. These organic-inorganic hybrids upon carbothermal reduction produce silicon carbide which is one of the strong material that is chemically and biologically inert in nature. Similarly, sol gel technique was used to derive titania nanoparticles that were used to develop photo catalysts used for decontamination of water.

Keywords : Sol gel technology, nanomaterial, nanocomposites, water treatment

Time-resolved Fluorescence Up-Conversion Study of Radiative Recombination Dynamics in III-Nitride Light Emitting Diodes over a Wide Bias Range

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Abstract: The technique of femtosecond fluorescence up-conversion was employed, for the first time, to explore the transient photoluminescence (PL) and carrier decay dynamics in c-plane (In,Ga)N MQW LEDs over a wide bias range. By investigating the bias dependence of initial transient photoluminescence (PL) intensity and the luminescence lifetime, the field and carrier density effects on the radiative recombination process were revealed for both low and high current injection conditions, and in good agreement with the theory.

Exploring Microstructures of Materials Using Ultra-Small-Angle Neutron Scattering

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Abstract. Modern materials science and engineering relies increasingly on detailed knowledge of the microstructure and interactions in soft and hard materials. Contemporary research areas comprise, e.g., biology and the life sciences, porosity, particle sizes as well as complex fluids. At the Australian Nuclear Science and Technology Organisation (ANSTO) the ultra-small-angle neutron scattering (USANS) instrument KOOKABURRA advances large-scale structure determination of complex systems of interest in the size range of 0.1 μm to 10 μm . USANS provides information on bulk properties with minimum sample preparation, and can be used to analyse material in a non-destructive manner.

Keywords. Neutrons, small-angle-scattering, ultra-small-angle scattering, microstructures

Electrospun Carbon Nanofibers and Their Applications

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Abstract. Electrospun carbon nanofibers are generally prepared through heat treatments (*e.g.*, stabilization, carbonization, and chlorination) of their precursors including, but not limited to, electrospun nanofibers of polyacrylonitrile, polyvinyl alcohol, lignin, and TiC. Unlike carbon nanotubes/nanofibers that are produced by bottom-up synthetic methods, electrospun carbon nanofibers are produced through a top-down manufacturing process; this results in low-cost, and more importantly, continuous nanofibers that are easy to align, assemble, and process into applications. In this talk, our recent studies on two types of electrospun carbon nanofibers (with either superior mechanical strength or high specific surface area) and their various applications will be presented [1-24].

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Acoustic Wannier-Stark ladders and Bloch oscillations in porous silicon multilayer structures

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We report the theoretical calculations and the experimental demonstration of Bloch oscillations and Wannier-Stark ladders for acoustic waves in multilayer structures based on porous silicon (PS). We designed and fabricated a structure with an acoustic band gap centered around 1.1 GHz. In order to tilt the initial acoustic band gap, we introduced a linear gradient in the acoustical parameter $\eta(z) = 1/v_L^2$ along the growth direction. Here v_L is sound longitudinal velocity of sound in bulk silicon along the (100) crystallographic direction. The purpose of this gradient is to mimic the effect of an external electric field on a semiconductor superlattice. By this way, acoustic Wannier-Stark ladders, i. e., a set of equidistant frequency levels, are obtained, and they are experimentally confirmed by measuring the transmission spectrum around 1.2 GHz. We measure the acoustic transmission spectrum in frequency domain, and by using the Fourier transform, we obtain the transmission spectrum in time domain. The spectrum of the fabricated sample shows acoustic Bloch oscillations with a period of 37 ns. The experimental results are in good agreement with the theoretical calculations obtained using the transfer matrix method. This phenomenon is the acoustic counterpart of the well-known electronic Bloch oscillations.

Keywords: Wannier-Stark ladders, Bloch oscillations, porous silicon, phononic crystals

Acknowledgments

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The Microcrystals Engineering using Self-organized Assemblies of Protonated meso-Tetraphenylporphine Dimers with the Help of Zundel cations, H_5O_2^+

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Properties of protonated meso-tetraphenylporphine (TPP) assemblies, as produced in aqueous tetrahydrofuran (THF) in the presence of HCl were investigated by UV-Vis, IR spectroscopy and atomic force microscopy (AFM) in thin films, and also the crystals obtained by light microscopy.

As found in this work initially produced aggregates can be destroyed by a strong shaking after that only di-protonated TPP dimers with $\lambda_{\text{max}} = 419$ nm of Soret band are observed in Fig. 1, curve 2. Restrictively protonated dimers are formed because of stronger hydrogen bonding due to H_5O_2^+ in a hydration shell around the dimers that repulses excess of the ions. Study of the aggregates in thin films by IR spectroscopy manifests a characteristic doublet at 1000 cm^{-1} arisen from H_5O_2^+ . A 454 cm^{-1} red shift of the 2766 cm^{-1} band arisen from N-H groups of pyrrole rings relative to the usual location at 3216 cm^{-1} indicates a 7.0 kcal mol^{-1} stronger hydrogen bonding in the clusters between TPP units of the dimers. The rods of width within 100-300 nm and up to 10 μm in the length are found in thin films of the di-protonated TPP assemblies by contact AFM. Crystallization of these rods occurs in thin films under relative humidity of 60% or higher. The size of the green crystals shown in Fig. 2 is varied within 30-35 μm . A “swallow” tail marked by red arrow that is often seen in the crystals implies a definite way of their formation associated with protons moving in the precursors. The crystals of 2-2.5 μm marked by a white arrow are usually spread over the whole field of the film. Assemblies of mainly mono-protonated TPP dimers, the spectrum of which is shown in Fig. 1, curve 3, produce these crystals. This work has been supported by the Deutscher Akademischer Austauschdienst (DAAD), Ref. 325, Kennziffer: A/01/06685.

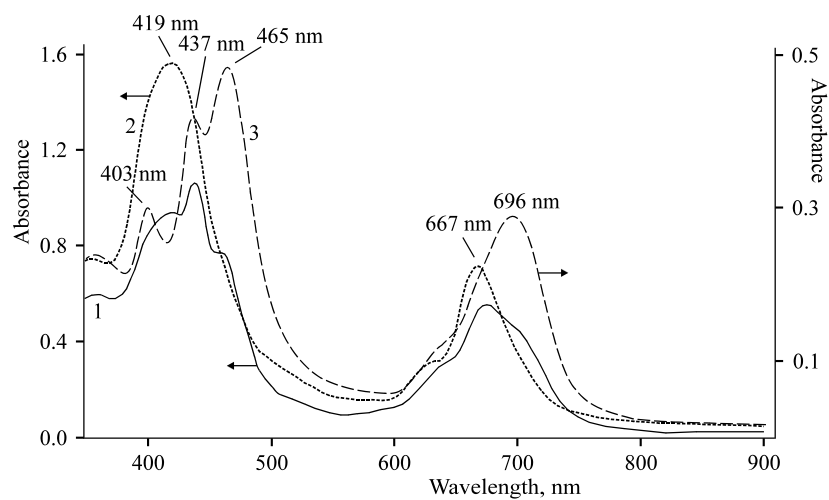


Fig. 1. Electronic absorption spectra of protonated TPP assemblies (1) in 2 N aqueous HCl and (2) after the assemblies destroying (left scale); and (3) in 0.8 N aqueous HCl (right scale) with 0.86 mol l^{-1} THF at the final TPP concentration of ca. $3.0 \times 10^{-5} \text{ mol l}^{-1}$. The optical pathway of the solutions was 0.2 cm.

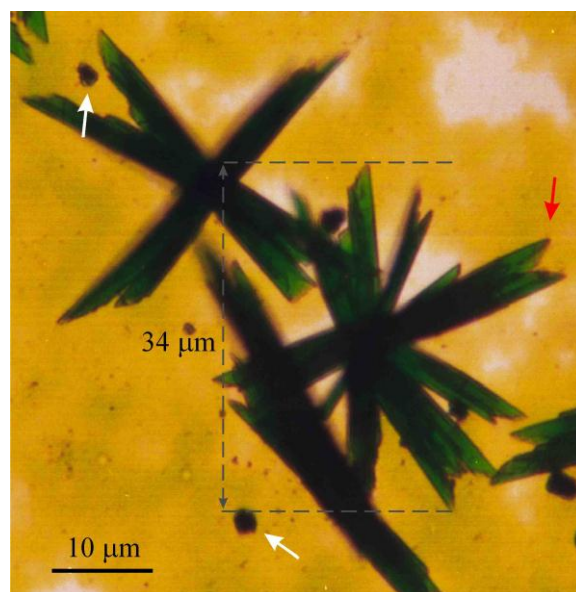


Fig. 2. Microphotograph of crystals obtained from assemblies of di-protonated TPP dimers with a light Zeiss microscope at 400-fold magnification.

EARTH STRUCTURE AND ROLE OF URANIUM IN THE ARCHITECTURE OF PLANETS AND SATELLITES

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ABSTRACT.At the centre of the earth, there was a sphere of polymerized water with carbon about 100 km in radius but it is not there anymore. Now there is an innermost core of solid elements that did not melt at the core temperature and have density more than that of molten copper. The innermost core is surrounded by a shell of molten copper. The vibrations of the innermost core are reflected outside by the anomalous 26 second microseisms recorded by Holcomb in 1983. The radius R of the vibrating sphere is calculated from a theoretical relation relating the radius with the velocity of shear waves and the time period of the vibration, it is 33 km. From the amount of copper released from the chondrites that built the earth along with irons. The calculated outer radius of the shell of molten copper is 156km. The entire shell was formed at a temperature around 1500K of the molten silicates. Later the copper shell slides to the centre where the temperature is about 6500K causing it to have thermal expansion and the outer radius of the shell would now reach 279km. The outer limit has now figured in the oceanographic experiments by Ishi and Dziewonsky of the geology department of the Harvard university when they investigated the nature of the deep around 300kms from the centre of the earth. The copper shell is surrounded by the Nickel-iron alloy extending to the outer limit of the solid iron core or 12 16 km from the centre as determined from travel time data of the earth quake waves. The structural shells outside the solid iron shell are the same as mentioned in the text books from travel time data. Next is the liquid iron alloy shell and then the mantle and the crust.

The earth scientists now agree that there does not exist a geodynamo, the author has advanced a theory to produce the dipole field using the paramagnetism of the large iron shell excited by the nuclear magnetic moment of the ^3He atoms produced by the nuclear explosions, which collect over liquid copper. Magnetic reversals are possible since there are two isotopes of helium that participate in collisions which degenerate alignment, or create fresh one, of the atomic dipoles. The evidence of existence of helium deep inside the earth is seen in the oozing out of helium from earth at many places.

Comparison of Single Yarn Distribution in Cross-Section of Water-Tempered and Non-Treated Ply Yarn

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Abstract. Warp yarn is one of the important elements of Persian carpet structure, and has a strong effect on its mechanical properties during and after weaving. The aim of this research is to investigate effect of water tempering on cross-sectional structure of carpet warp yarn.

In this research 31.4/6 and 31.4/9 ply cotton yarns water temper finished according to the method used in Naein city of Esfahan of Iran for Naein carpets. Large skeins of warp yarn were scoured and stored loosely in water for 5 hours (scoured). The skeins were removed from water and beaten on a flat surface with a flat wooden bat (water tempered). Then they were stretched by 7.5% and left to dry at that tension. Five groups of ply yarns were examined as follow:

1- The basic yarn, 2- scoured, 3- scoured and water tempered, 4- scoured in water and detergent, 5- scoured in water and detergent and tempered. Samples 1 to 5 were for 6 ply yarn and 6 to 10 for 9 ply yarns.

The yarns were molded in polyester resin, sliced in cross-sectional direction, and photographed under microscope with a magnification of 100 xs. The images were given a color shade from black to white with Photoshop program and were analyzed with a program written in MATLAB environment. In this program boundaries of ply yarn and each single yarn, center of gravity of ply and single yarns and distance of each single yarn from center of the ply yarn were measured. They were used for calculation of area of single yarns, ply yarns and empty spaces in cross-section of the ply yarns. Figures 1 and 2 show areas of ply yarns and empty spaces in cross-section of the yarns respectively. Figure 1 shows that, area of water tempered yarn (3) is higher than other 6 ply yarns. Addition of detergent in tempering allows better space allocation of single yarns in ply yarn structure due to lower friction and reduces yarn volume. This corresponds with the results of empty spaces between single yarns in ply yarn structures shown in figure 2. The same trend happens for 9 ply yarn. It may be concluded that, water tempering increases volume of the yarn in comparison to the base yarn and releases some of the internal tensions of the yarn, which is beneficial for carpet structure and may affect behavior of the warp yarn under tension during weaving.

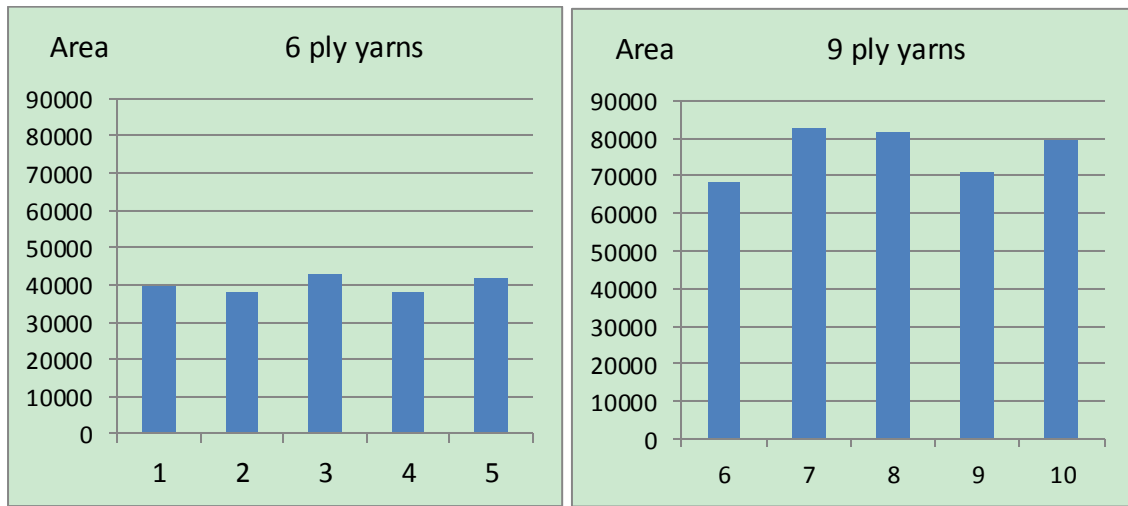


Figure 1. Area of the yarns in arbitrary unit for ply yarns

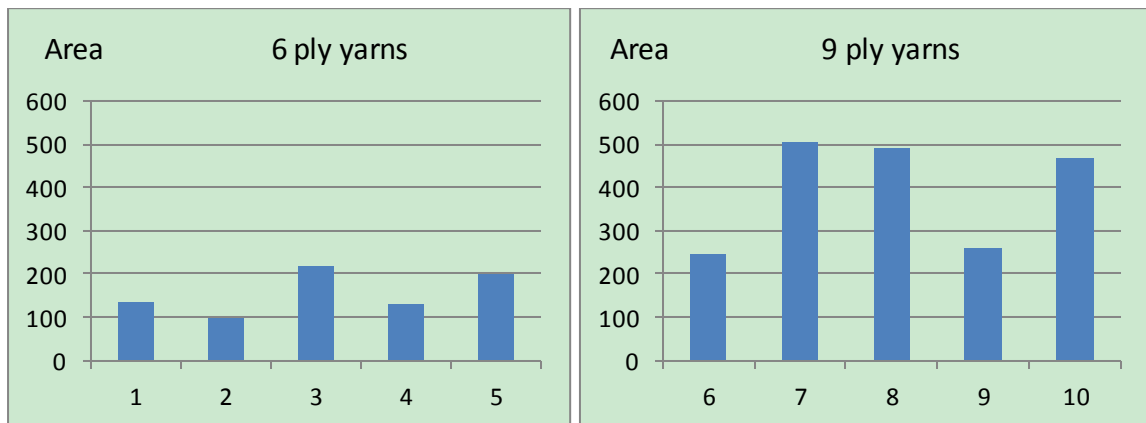


Figure 2. Area of the empty spaces between the yarns in arbitrary unit

Magnetism and spin transport through transition metal organometallic molecules

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Transition metal organometallics has recently attracted much attention due to its potential for applications in catalysis, polymers, molecular recognition, high-density storage, quantum computing, and spintronics. Despite these applications, reliable theoretical and experimental knowledge of energetics, dissociation energy, spin multiplicity, spin gaps, etc. of these systems is still missing. Therefore we have performed very accurate fixed-node quantum Monte Carlo (QMC) calculations [1] with the quest to elucidate electronic and atomic structure of these systems and thus to provide ultimate answers to the open questions.

Taking vanadium-benzene half-sandwich as an example [2], we find, at variance with DFT results which favor either low- or high-spin state, depending on the functional used, QMC predicts degenerate energies for spin multiplicities 2, 4, and 6, irrespective of DFT functional used to fix the nodal hyper-surfaces. Our QMC results indicate that both DFT as well as experimental results may be strongly biased.

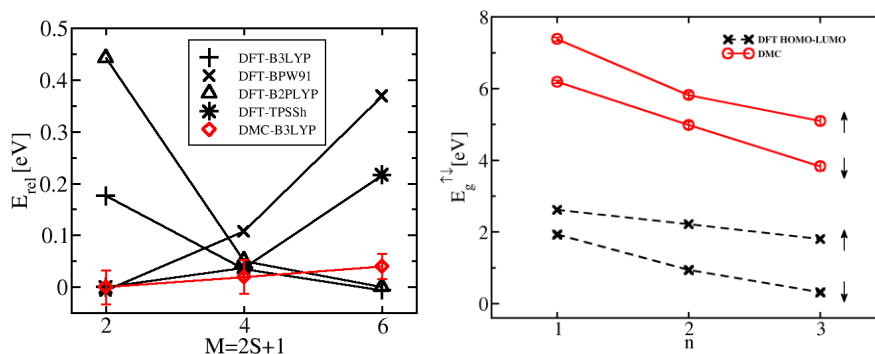


Figure. Left: spin multiplicity of vanadium benzene half-sandwich in QMC and various DFT treatments. Right: $\uparrow/\downarrow$ -spin gaps for vanadium-benzene full sandwich structures in DFT and QMC treatments.

We have also studied full-sandwich vanadium-benzene multi-decker clusters, V_nBz_{n+1} , $n = 1-3$ [3]. The most important prospective applications of these and related systems was predicted in spintronics as spin filters. Use as spin filters requires them to be half-metal ferromagnets, in order to feature a metallic gap for the minority-spin electrons and semiconducting gaps for the majority-spin electrons. We find that while magnetic structure of these systems is consistent with ferromagnetic coupling, their electronic structure is not consistent with half-metallic behavior as previously assumed, but rather this system is a ferromagnetic insulator with large and broadly similar $\uparrow/\downarrow$ -spin gaps, implying thus a

limited potential of these and related materials for spintronic applications unless they are further modified or functionalized.

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Two-ply material with anisotropic substrate

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Abstract. This report presents on the method of formation of tungsten layer on the graphite surface. The described method can be used to create powerful anode x-ray tubes for medical purposes.

Keywords: Tungsten, Graphite, CVD, X-ray tube anode.

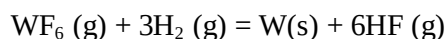
1. Introduction

Modern development of electro-vacuum technology requires the use of new materials and special alloys that meet the specified requirements. Refractory materials today are received prevalence, particularly tungsten. Tungsten is used both independently and as coatings paired with other materials. Formation of the tungsten coating on the graphite surface is promising.

2. Results and discussion

The main advantage of crystallisation from the gas phase is that the deposition takes place at the atomic level. This allows to obtain a refractory material having a density close to the theoretical value. Coating may be applied to any form of product. The starting material for the coating is tungsten hexafluoride.

Reacting tungsten hexafluoride with hydrogen is described overall equation:



Close coefficients of thermal linear expansion are required for such pair of high-temperature materials. As it will be seen at figure 1, it is advisable to use graphite $\alpha \perp$ as the substrate on which it will be precipitation. In that case the difference in coefficients of thermal linear expansion of materials does not exceed $2 \cdot 10^{-6} \text{ K}^{-1}$.

Removal of heat efficiency is an important task for products operating at high temperature. Reset of heat is possible by thermal conductivity (fig. 2) and the emission from the surface. Coefficient of thermal conductivity of polycrystalline tungsten linearly decreases with increasing temperature. Thermal conductivity varies from 104 to 90 W/m/°C when the temperature changes from 1200 to

2400 °C. The emissivity increases monotonically in the temperature range 1200-2200 °C and it is 10-15% higher in comparison with the reference data.

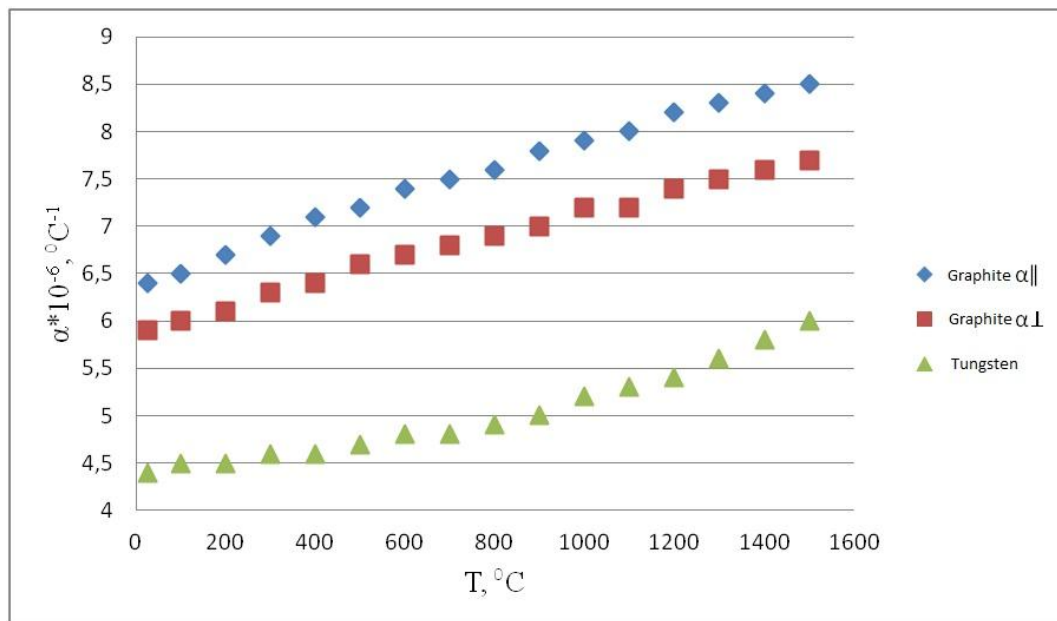


Fig. 1. Coefficient of linear thermal expansion

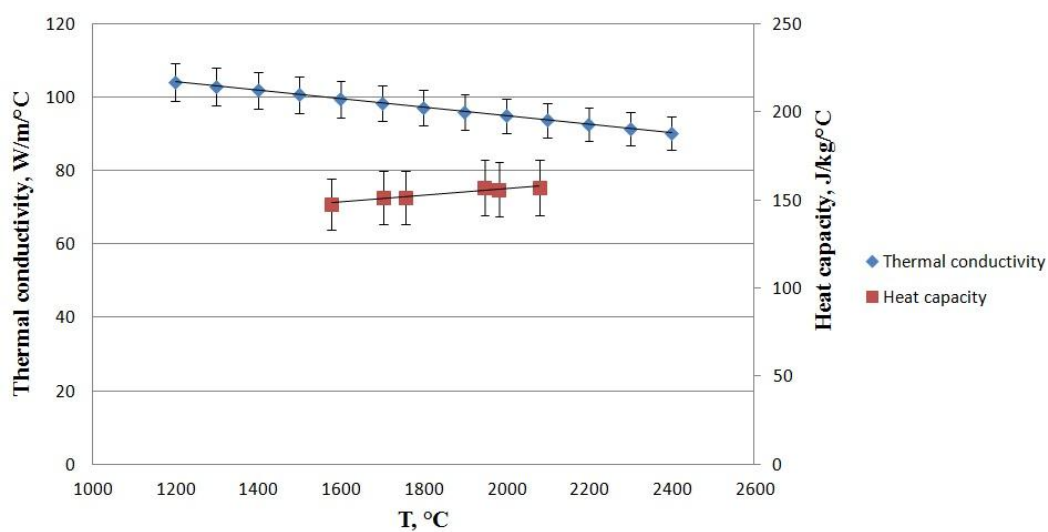


Fig. 2. Heat capacity and thermal conductivity of tungsten

The measured values of the heat capacity are shown in figure 2. It is shown that the heat capacity of the polycrystalline tungsten is in the range of 130-160 J/kg/°C when the temperature changes from 1500 to 2100 °C.

After deposition, the sample was portioned into several pieces for metallographic analysis. The surface topography of tungsten coating is 40 microns. Quality of adhesion applied layer to the substrate is good. Open pores, cavities and cracks on the boundary of tungsten-graphite haven't been

detected. As a result of precipitation precipitate was formed with a columnar structure (fig. 3), high density and the presence of a certain texture of growth. The initial layers of precipitated tungsten are composed of small grains ($\leq 1 \text{ mm}$) and it is indicated the presence plurality of centers of crystallization. With further precipitation occurs preferential development of the embryos, the orientation of which proved the most thermodynamically favorable - tops in the growth direction. At the same time, oriented crystals stop the development when their top touches neighboring crystal.

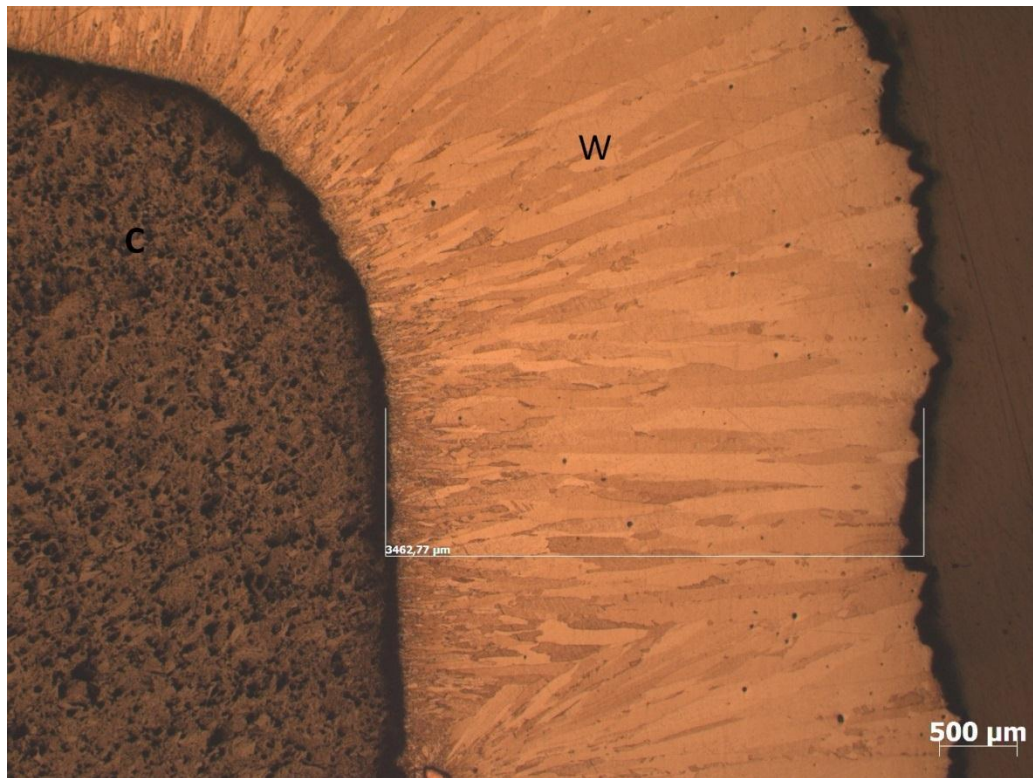


Fig. 3. Structure of the deposited coating

Series of annealing was conducted in a case of determination the rate of growth the carbide layer on the border of tungsten and graphite from a temperature. Value of the carbide layer was 10 microns at $T = 1400^\circ \text{C}$ and the time of 5 hours, and 100 microns at $T = 1700^\circ \text{C}$ and the time of 1 hour.

Strength tests were conducted in a case of determination the influence degree of carbide layer to strength characteristics of tungsten-graphite layer.

3. Summary

1. The layer of polycrystalline tungsten was applied on the surface of the graphite by CVD method. It is shown that due to the thermo physical properties of graphite and tungsten, these materials can effectively work together at temperatures up to 2200°C . The structure of the precipitated material and the quality of the adhesion of base and inflicted tungsten layer was investigated.

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Synthesis and characterization of CuO/NiCo₂O₄ core/shell nanowire arrays directly grown on copper foam

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Abstract: A two-step solution method followed by a heat treatment process is developed for the synthesis of novel nanoscale core/shell hetero-structures with CuO nanowires as the core and NiCo₂O₄ nanoneedles as the shell directly grown on copper foam. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are used to investigate and analyze the resulting hetero-structures. The results indicate that the secondary growth of NiCo₂O₄ nanoneedles around CuO nanowires leads to the formation of CuO/NiCo₂O₄ hetero-hierarchical core/shell nanowire arrays.

Keywords: CuO/NiCo₂O₄ core/shell; nanowire arrays; synthesis and characterization

1. Introduction

One-dimensional (1D) hetero-structured nanomaterials are the focus of recent scientific and technological interests because they play an important role as essential components in various nanoscale devices, including electronics, optoelectronics, chemical/bio/optical sensors/detectors, and energy harvesting/conversion devices.¹⁻³ Great efforts have been directly devoted to the development of new synthetic strategies for fabrication of novel core/shell nanowire hetero-structures with well-controlled sizes and shapes.^{2,3} Thus far, a great variety of hetero-structures with core/shell nanowire feature and fascinating properties have been demonstrated. However, it is still of great challenge but highly desirable for the rational design and facile synthesis of core/shell nanowire hetero-structures with well-defined morphologies and tunable functions in a large scale at low-cost.^{1,4-6}

Compared to physical strategies, the solution-based techniques are regarded as low-cost effective approaches in preparing various nanostructures with good control of shape, composition and reproducibility together with the advantages of low growth temperature, environmental friendliness, and process simplicity.³

Transition metal oxides are vitally important for the development of various novel materials with functionality and smartness.² Among them, CuO and NiCo₂O₄ have been intensively studied separately for many applications in different areas ranging from lithium ion batteries, gas sensors, energetic materials, and supercapacitor (SC).^{3,7,8}

In this work, we introduce a simple two-step solution method followed by a heat treatment process to smartly integrate CuO nanowires with NiCo₂O₄ nanoneedles to form novel CuO/NiCo₂O₄ core/shell nanowire arrays that are directly grown on copper foam.

2. Experimental Section

2.1. Synthesis of CuO nanowires on copper foam

The copper foam with a thickness of 0.5 mm (110 PPI) from Changsha Lyrin New Materials Co. Ltd is used as substrate for the preparation of CuO nanowires. The copper foam is cleaned for 30 s in a solution composed of 10 ml HCl (37%) and 120 ml deionized (DI) water to remove the native oxide on the copper surface. It is then adequately rinsed with DI water and blow dried by compressed air. The as-cleaned copper foam with 7 cm in length and 7cm in width was immersed in a mixed aqueous solution of 2.5 M sodium hydroxide and 0.1 M ammonium persulphate at room temperature for about 20 min. Subsequently, the as-prepared Cu foam was taken out of the solution and fully rinsed with distilled water for several times, followed by drying in a nitrogen stream. Finally, it was annealed at 120 °C for 2 h and then maintained at 180 °C for 2 h in Argon gas.

2.2. Synthesis of hierarchical CuO/NiCo₂O₄ core/shell nanowire arrays

The as-obtained CuO nanowires on Cu foam were immersed in mixed solution by chemical bath deposition according to the procedure reported in our previous paper.⁷ The substrates were then taken out from the solution, rinsed with distilled water, and ultrasonically cleaned in alcohol for several times followed by annealing at 300 °C in normal argon gas for 1.5 h to prepare hierarchical CuO/NiCo₂O₄ core/shell nanowire arrays on Cu foam.

3. Results and Discussion

The SEM analysis of the morphologies of CuO nanowire arrays before and after the deposition of NiCo_2O_4 is shown in Figure 1. From Figure 1(a), it is evident that large-scale CuO nanowires are uniformly covered on the surface of copper foam, forming a nanoarray configuration. The SEM image with a higher magnification shown in Figure 1(b) demonstrates that these CuO nanowires grow approximately perpendicularly aligned on copper foam surface. The CuO nanowires have relatively rough surfaces with a diameter in the range of 100-400 nm. After the deposition of NiCo_2O_4 nanoneedles, the uniform array structure is still well retained and numerous ultrathin branched NiCo_2O_4 nanoneedles decorate on the CuO nanowire surfaces as can be seen in Figure 1(c). A magnified SEM image shown in Figure 1(d) reveals that the NiCo_2O_4 nanoneedles shells are fully coated on the CuO core with good uniformity and grow fairly homogenous along the CuO nanoarray core, forming 3D core/shell architecture with a highly open structure on a large scale, indicating the intimate interface contact between CuO nanowires core and branched NiCo_2O_4 nanosheet shells. The formation of branched NiCo_2O_4 nanosheets is believed to be attributed to “oriented attachment” and “self-assembly” processes.⁷

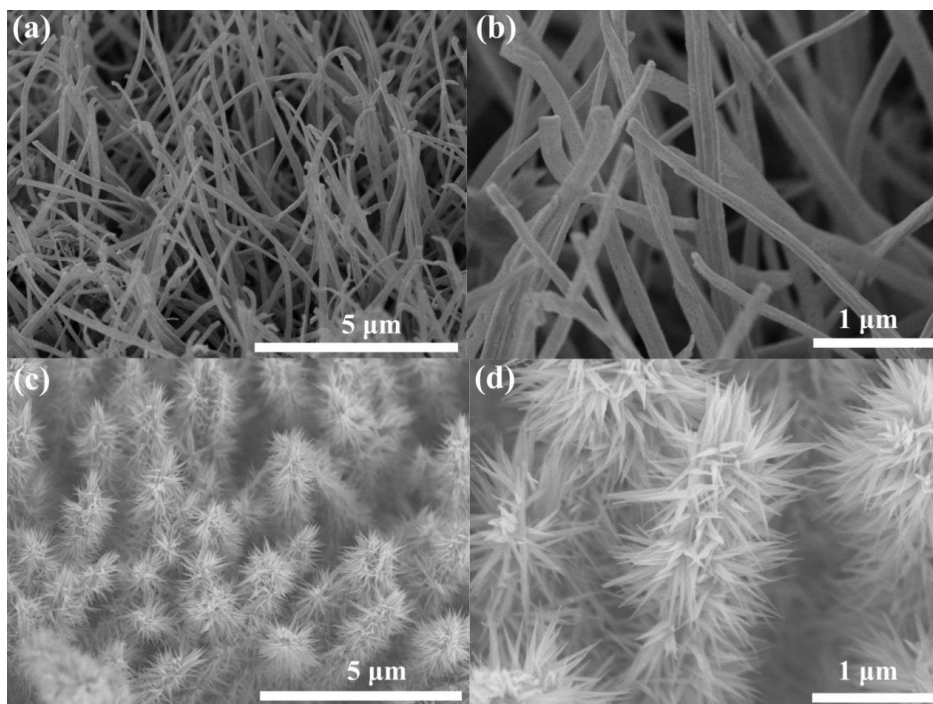


Figure 1. SEM images of CuO nanowires (a-b) and hierarchical CuO/ NiCo_2O_4 core/shell nanowire arrays (c-d) on Cu foam.

The detailed microstructure of hierarchical CuO/NiCo₂O₄ core/shell heterostructure is further investigated by TEM and HRTEM. From Figure 2(a), it is evidently observed that numerous highly uniform tiny NiCo₂O₄ nanoneedles are successfully covered on the surface of CuO nanowires, which is in accordance well with the SEM results. The magnified TEM image shown in Figure 2(b) demonstrates that NiCo₂O₄ nanoneedles are in fact composed by many small nanoparticles. HRTEM in Figure 2(c) shows clear fringes with a measured interplanar spacing of 0.24 nm, corresponding to interplanar distance of the (311) of NiCo₂O₄,⁹ which is further confirmed by its corresponding fast fourier transform pattern shown in the inset of Figure 3(c), indicating the formation of NiCo₂O₄ nanoneedle shells on the surface of CuO nanowires. The STEM line-scan results as illustrated in Figure 2(d), in which only elements of Cu, Co, Ni and O are detected with carbon element coming from the support, further confirm the successful formation of CuO/NiCo₂O₄ core/shell heterostructures.

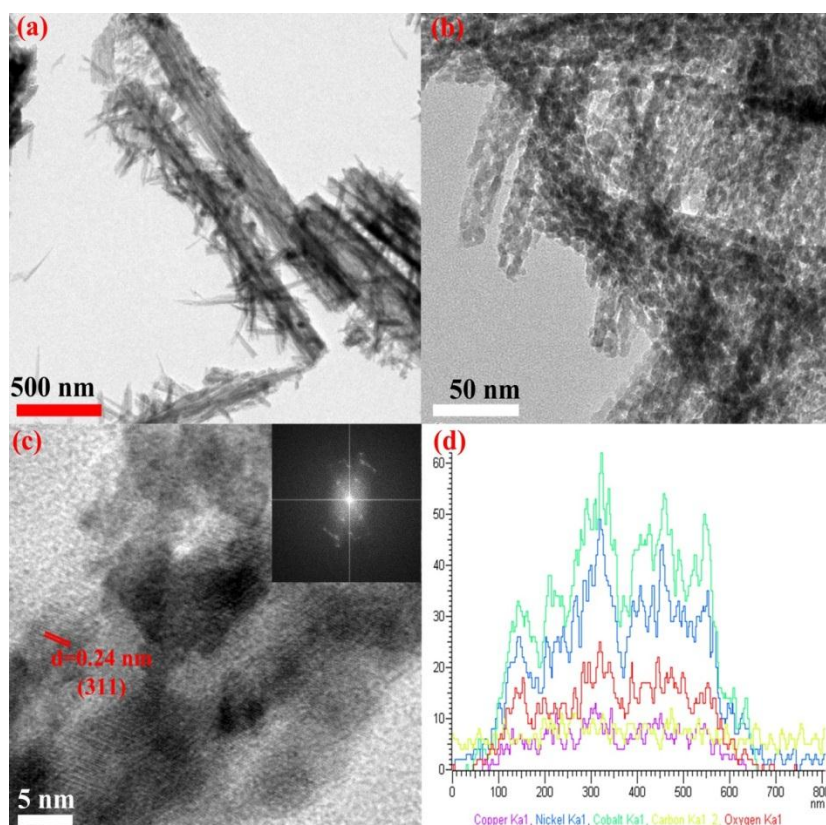


Figure 2. TEM images of (a) CuO/NiCo₂O₄ core/shell heterostructure and (b) NiCo₂O₄ nanoneedles, (c) HRTEM image of NiCo₂O₄ nanoneedle (inset is its corresponding fast fourier transform pattern), and (d) STEM line-scan spectra distribution of CuO/NiCo₂O₄ core/shell heterostructures.

4. Conclusion

In summary, hierarchical CuO/NiCo₂O₄ core/shell nanowire arrays have been successfully synthesized on copper foam by a simple two-step solution growth method followed by a calcination process. SEM results demonstrate that NiCo₂O₄ nanoneedles shells are fully coated on the CuO nanowires core with good uniformity and grow fairly homogenous along the CuO nanowires core, forming the core/shell architecture. TEM results show that the NiCo₂O₄ nanoneedles shells are in fact composed by many small nanoparticles. This work paves a new way for effectively designing hierarchical core/shell nanowire array structures on substrates by employing straightforward chemical synthesis routines. The as-prepared hierarchical CuO/NiCo₂O₄ core/shell nanowire arrays on Cu foam have promising applications in different areas such as lithium ion batteries, gas sensors, energetic materials, and supercapacitors.

4.1. Acknowledgment

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Forming of new thermoplastic based fibre metal laminates

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Abstract: The main advantage concerning the development of so-called fibre metal laminates (combination of fibre-reinforced plastics with metals) is the interaction of a high specific strength and moderate ductility. One option towards the further development of the well-known fibre metal laminates (e.g. GLARE) is the substitution of the thermosetting resin with a thermoplastic matrix. The advantages of these new compounds are the short cycle time and the formability with heated tools. Hybrid laminates consisting of fibre-reinforced polyamide and aluminium were investigated. A reproducible interface engineering with a very good adhesion is essential for a successful consolidation of these innovative fibre metal laminates. Therefore, different surface modification methods were studied. The forming behaviour of the fibre metal laminates was investigated with the v-bending and deep drawing operations. The forming result depends mainly on the temperature relating to thermoplastic matrix.

Keywords: fibre metal laminates, thermoplastic matrix, hybrid compounds, interface engineering, forming

1. Introduction

Fibre- and textile-fibre-reinforced plastics (FRP) provide the highest potential of lightweight constructions. However, in different applications a defined ductility is necessary. To obtain these requirements, metal foils and fibre-reinforced plastics were combined in to hybrid laminates or so-called fibre metal laminates. To improve the light-weight construction properties and the damage tolerance, hybrid laminates with continuous fibre-reinforced thermosetting plastic matrix layers have been developed. Different activities are dealing with the materials GLARE (glass-fibre-reinforced plastics/aluminium foil laminate), ARALL (aramid-fibre-reinforced plastics/ aluminium foil laminate), CARALL (carbon-fibre-reinforced plastics/aluminium foil laminate) and TiGr (titanium-graphite laminate) [1-3].

New investigations show hybrid laminates with thermoplastic matrices. Advantages like an attractive price, better recycling, large scale manufacturing and the formability can be offered in comparison to thermosetting plastics. This paper is dealing with the investigation of the formability of these new thermoplastic hybrid laminates consisting of aluminium alloy sheets (EN AW-6082) and carbon fibre-reinforced polyamide 6 (CF-PA6).

2. Experimental details

2.1. Semi-finished prepregs

The first step of the process is the production of thermoplastic pre-impregnated unidirectional (UD) fibre semi-finished products using the prototype UD fibre foil tape unit (FFTU). The FFTU is working on the basis of the continuous process of the fibre ribbon technology. This new technology allows the direct processing of fibre filaments with plastic films in a fibre-friendly process step to form semi-finished products with fully extended and damage-free embedded fibres in the matrix material. To obtain the fibre-film ribbons, a very good spread of the individual fibre filaments and a minimum number of filament layers is achieved to ensure short flow paths of the molten thermoplast in the consolidation process. Detailed information about the FFTU-process are shown e.g. in [4-7].

2.2. Interface engineering

To obtain adequate properties an appropriate interface engineering between the metal and the thermoplastic FRP is essential. Therefore, a suitable surface treatment of the metal component is necessary. Different treatment methods were compared, e.g.: mechanical blasting, plasma electrolytic anodic oxidation, chemical treatment and twin polymers regarding the achieved shear strength in the interface FRP and metal. Additional information about these surface treatments and the obtained shear strength are shown e.g. in [6, 7]. By means of the boundary conditions (e.g. thickness of the aluminium alloy layer, manageability, efficiency, suitability for large scales and series production) and the achieved shear strength mechanical blasting was selected for the presented investigations. Nevertheless, this method is limited suitable for the forming process caused by the high roughness in contact with the forming tool.

2.3. Consolidation of hybrid laminates

The preparation of the hybrid laminates by means of the pre impregnated fibre-foil-ribbons occurs by the directly pressing with the treated aluminium alloy foils (see Figure 1) at a mould temperature of 285 °C in a pressure process (1 MPa pre pressure for 11 min, 1.5 MPa consolidation pressure for 3 min and 0.5 MPa post pressure for 14 min) and removing after cooling to approximately room temperature (see e.g. [4, 5]). These parameters were selected to obtain a satisfactory impregnation of the fibre-foil-ribbons as well as an adequate consolidation with the metal layers. Moreover, it is important to avoid matrix degradation at too high temperatures, fibre displacements and fibre damages or pressed out matrix material.

The hybrid laminates are configured alternating with two metallic layers and one fibre-reinforced layer consisting of four single fibre-foil-ribbons to so called 2/1-hybrid laminates. The top layers consist of the aluminium alloy foils. The fibre-reinforced layer exhibits a thickness of approximately 0.7 mm. The aluminium alloy foil display a thickness of 0.5 mm, see Figure 1.

2.4. Forming of the hybrid laminates

The forming results from fibre laminates with thermoplastic matrix are significantly affected by the temperature [8]. Therefore the tools in Figure 2 were used to form the explained hybrid laminates. The v-bending and deep drawing parameters are listed in Table 1.

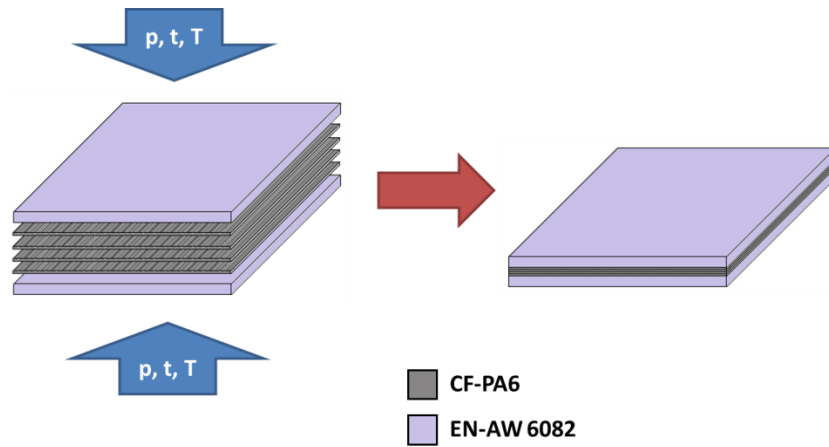


Figure 1: Hybrid laminates (schematic representation)

Table 1: forming parameters

v-bending		deep drawing	
bending radius [mm]	1; 5	punch diameter [mm]	100
temperature for blank and die [°C]	180 - 250	temperature for blank, blank holder and punch [°C]	180 - 220
the fibre direction to the bending axis [°]	0; 90	blank holder force [kN]	20; 100 - 800

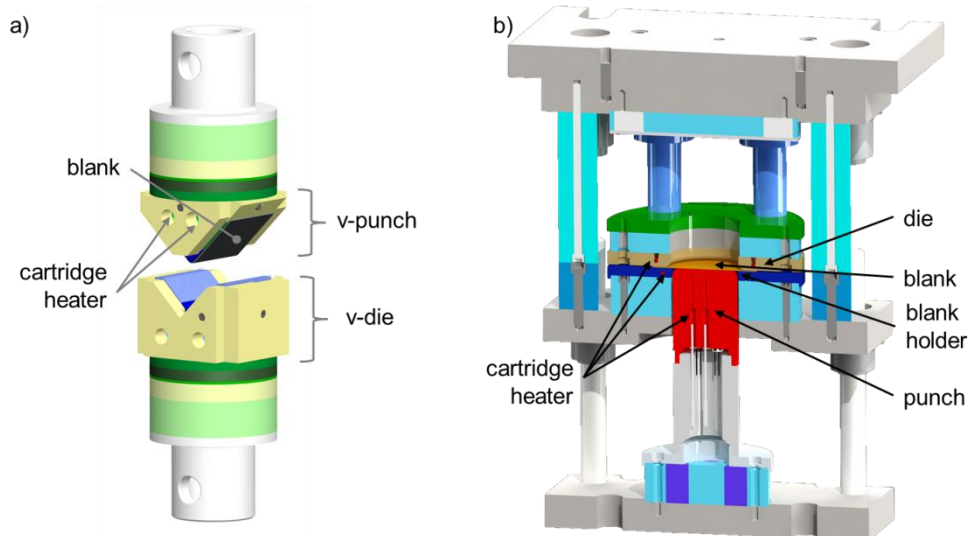


Figure 2: Heated forming tools to form hybrid laminates: a) v bending, b) deep drawing

For the v-bending both tool parts are heated with cartridges. Two bending radii ($r_5 = 5$ mm and $r_1 = 1$ mm) related to different forming temperatures (180 - 250 °C) were analysed. By forming at temperature lower than 180 °C cracks in laminate occur and by using temperature beyond 220 °C the polymer matrix is pressed out of the laminate. After forming the springback coefficient (see equation 1) was captured to evaluate the forming result. This coefficient is the relation between the angles at the work piece (α_2) and the tool (α_1).

$$k = \frac{\alpha_2}{\alpha_1} \quad (1)$$

The deep drawing tool which was used to determinate the drawing ratio with no cracks and wrinkles is presented in Figure 2 b. The drawing ratio is defined through the relation between the diameters of the blank (d_0) and the punch (d_1), see equation 2.

$$\beta = \frac{d_0}{d_1} \quad (2)$$

In addition to the forming temperature (180 – 220 °C) the blankholder force as a very important parameter was varied. Constrained by the press, the blankholder force maximum is 800 kN, see Table 1.

3. Results and Discussion

3.1. Production of fibre-reinforced thermoplastic semi-finished products

Within the FFTU it was possible to reach a significant fibre roving spread of the carbon fibres of 6 mm to 11 mm. The spreaded rovings were covered by a thermoplastic film on both sides. Within the heating field the UD-tapes were pre-consolidated between the calendar rolls and wound on a driven roller. The rovings are well-spreaded without defects. A fibre volume content of 60 %, depending on the spreading and thickness of the thermoplastic foil (e.g. 30 µm), can be produced.

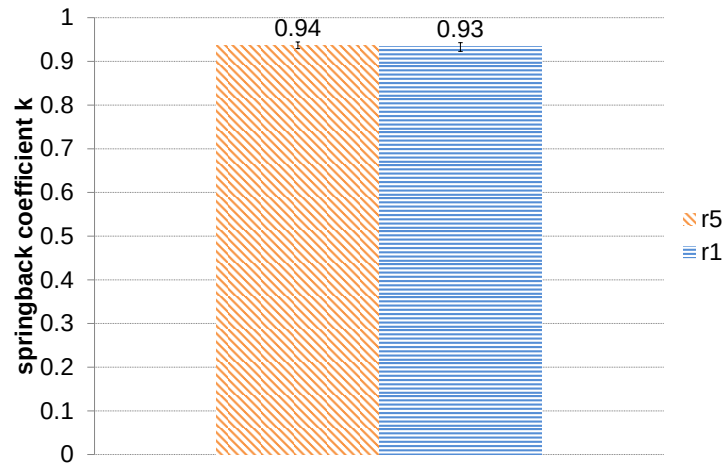


Figure 3: Diagram of the spring back coefficient depending on the bending radius $r_5 = 5$ mm and $r_1 = 1$ mm

3.2. Forming of the hybrid laminates

The consolidated hybrid laminates with the EN AW-6082 alloy foils and the CF-PA6-layers were tailored to different shapes for several forming experiments (v-bending and deep drawing). The analysed springback coefficient after v-bending shows that the coefficient k is near 1 ($k = 0.94$ for $r = 5$ mm) (see Figure 3). Hence, the springback behaviour of the laminate in comparison to bending a single aluminium blank ($k = 0.9$) is very small. Thus, after forming and cool down the thermoplastic

matrix the elastic tension of the aluminium layer is still present in the compound. Furthermore, the investigated parameters temperature and bending radius display no influence on the springback behaviour. The prepared micro section of a formed v-bending example (see Figure 4, bending orthogonal to the fibre direction, forming temperature 200 °C) shows no fibre cracks and no delamination between CF-PA6 and the aluminium alloy. Furthermore, Figure 4 displays a significant roughness for an adequate clamping of the thermoplastic matrix with the aluminium alloy foil. These results demonstrate the possibility of v-bending of the hybrid laminates orthogonal to the fibre direction without fibre fraction and delamination.

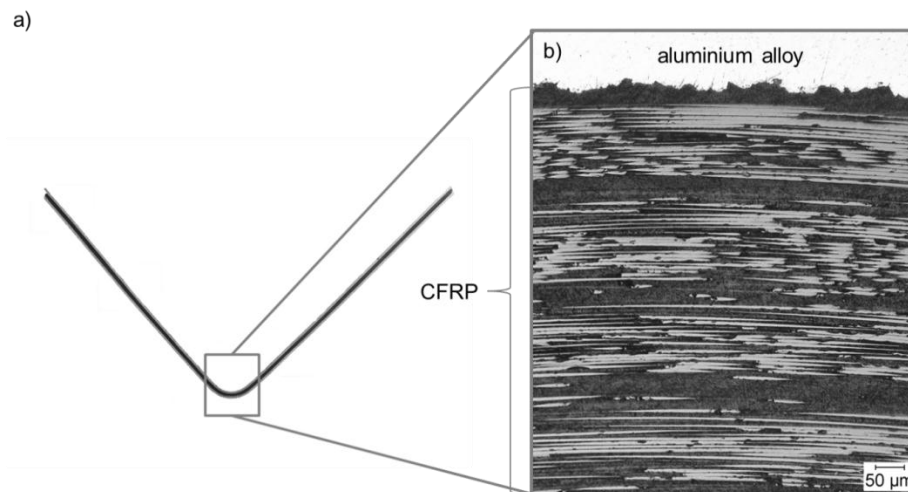


Figure 4: a) V-bending example (schematic representation), b) micro section of the bending radius

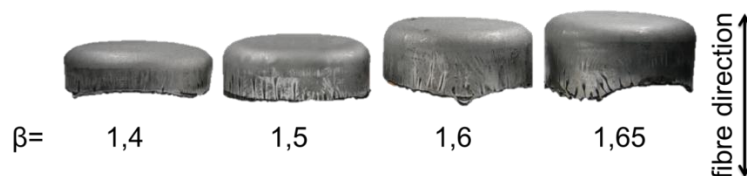


Figure 5: deep drawing result depending on the drawing ratio

The deep drawing investigations result in rotationally symmetric cups, see in Figure 5. Until a drawing ratio of 1.65 no cracks occur. However, at the flange of the cups wrinkles become apparent. The tendency towards wrinkling of the compound rises with increasing forming temperature. If the forming temperature is too low cracks in fibres occur. An optimum of the forming temperature depending on the blankholder force is an aim of further investigation. In spite of the roughness of the aluminium alloy foil in contact with the deep drawing tool, an adequate result can be obtained. The rotationally symmetric cups after the deep drawing process exhibit the possibility to form hybrid laminates, in addition to the above named v-bending results, with complex structures. Furthermore, investigations regarding different material compositions and combinations (e.g. 2/1- or 3/2-laminates, different thicknesses of the layers) as well as various surface treatment methods with an adapted roughness for a more comfortable forming process and an adequate interface are part of current investigations.

4. Conclusions and Outlook

By means of the presented results the advantage of forming of the thermoplastic hybrid laminates or fiber metal laminates in comparison to the thermosetting fiber metal laminates (e.g. GLARE) was demonstrated. The v-bending and deep-drawing investigations display the possibility to form simple and complex structures.

The v-bending tests display the possibility to form with different radii orthogonal to the fibre direction without fibre cracks and delamination. The measured springback of the fibre metal laminate is small. Therefore it must be noted that the elastic bending stresses were not degraded in the aluminium layer. Deep drawing investigations show no cracks until a drawing ratio of 1.65. It has been demonstrated that the forming temperature is in connection with the visible wrinkles at the flange of the cup. Further investigations of this relation are in progress.

Furthermore, it has been proven that the mechanical blasting is an efficient and useful method to treat the surface of the aluminium alloy foils for an adequate clamping of the thermoplast with the aluminium alloy and so an appropriate interface. To minimize the friction and to facilitate the forming process, further investigations are necessary to provide an adequate interface. Therefore an efficient treatment method with a suitable roughness of the aluminium foil in contact with the forming tool is necessary.

Investigations to form different hybrid laminates with various compositions (e.g. different fibres, thermoplastic matrices, metal components) as well as combinations (e.g. 2/1- or 3/2-laminates) and different thicknesses of the layers are part of current work.

Acknowledgement

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Mechanical and reological properties of polyurethane elastomers from hydroxy-terminated polybutadiene and isophorone diisocyanate used as liners for composite propellants

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Abstract. In this contribution we studied mechanical and reological properties of liners based on hydroxyterminated polybutadiene (HTPB) loaded with titanium dioxide and cured with isophorone diisocyanate (IPDI) or toluene diisocyanate (TDI). A thixotropic agent (Thixin R, NL Industries, U.S.) was added and viscosity was measured as a function of curing time, leading to much lower viscosities and longer pot life values. Mechanical properties (tensile strength and elongation at break) were not significantly affected but viscosity was reduced at all tested concentrations. Loss modulus (G'') and storage modulus (G') were measured during cure time at three different temperatures (7, 25 and 60 °C) with IPDI, and at 7 and 25 °C for TDI. Both curves did not intersected during the cure period studied (120 minutes) for IPDI but did so for TDI at 25 °C with the formulation having a thixotropic additive. These results suggested that liner formulations will flow if sprayed onto the inner surface of a rocket case before propellant is casted into.

1. Introduction

A liner for composite propellants is basically an elastomeric material applied between the insulation and the propellant to improve interface properties between insulator and propellant and to hold the propellant to the insulated motor case without debond in all the environmental conditions (1). The polyurethane-based elastomers on hydroxy-terminated polybutadiene (HTPB) are the polymers of choice when trying to secure a good bond to the propellant rocket motor body and at the same time to protect it from the high temperatures generated by burning the propellant (2). This last property is due to the fact that TiO_2 is added to the liner formulations.

Liners are usually applied by a spatula or spray on the inner face of the motor tube. In order to facilitate the application is common practice to dilute with dichloromethane in some proportion for facilitate the application onto the inner side of tubes (3). However, other approach is to add a thixotropic agent to increase the fluence of the liner without affecting its curing properties. In this

contribution, we studied the curing rate of liners containing a thixotropic agent and the rheological and mechanical properties of the resulting elastomers. Liners are cured with different isocyanates, which differ in its rate of reaction. Aliphatic isocyanates have a slower rate of cure than aromatic isocyanates (4). Rodić and Petrić (5) investigated the effect of the curing agent on the cure time ("pot life") of different liners compositions and on the properties of these liners for composite propellant formulations. Pot life was defined as the time necessary for the liner to reach a viscosity of 50.000 cps (6). Wingborg (7) studied the effect of polyol, curator and chain extender on the properties of propellant formulations. In this contribution, we studied the effect of a fast and slow cure isocyanate and a thixotropic additive onto the rheological and mechanical properties of liners, with the objective of determining its applicability by spraying onto metal rocket casings.

2. Materials and Methods

The HTPB has an average molecular weight of 2900 Daltons and a polydispersity index of 2.5. (Chinese origin). Toluidine diisocyanate (TDI) was obtained by donation from Petroquímica Ró Tercero (Argentina). The catalyst dibutyl tin laurate (DBTL) and isophorone diisocyanate (IPDI) were purchased from Sigma-Aldrich Corporation, U.S.. Commercial titanium dioxide was grounded to a diameter of 10-12 microns. Glyceryl monoricinoleate (MRG) was used as chain extending agent. To formulate the mixtures, all the ingredients were added to the polymer and then mixed with HTPB in vacuum (4 mm Hg) for 2 hours at 200 rpm with a Coules-type mixer. Finally the isocyanate was added together with the catalyst. To determine viscosity a "Brookfield" viscometer HBT model was used with different spindles and calculating values in centiPoisie (cps). Mechanical properties were studied by measuring hardness, tensile strength and elongation to break. Shore A hardness was measured with a DIGIMESS HT-6510 A penetrometer in triplicate on fully cured liner films (7 days of curing at ambient temperature) to check that values are within 50-70 units.

3. Results

3.1. Viscosity curves

Viscosity curves with toluidine diisocyanate (TDI) and in with isophorone diisocyanate (IPDI) were obtained. The aliphatic isocyanate IPDI is less reactive than aromatic TDI, so the curing time ("pot life") is longer (120 minutes versus 20 minutes when the mixture cures only with TDI). When the thixotropic agent Thixin R (NL Industries, U.S.) was added, viscosities were reduced, increasing fluence. The results are shown in the following Figure:

It was observed that the curves with IPDI in stoichiometric amount with OH of polyol (PBHT) groups and chain extended with MRG cured faster than the fast cure (6.2% of TDI) formulation.

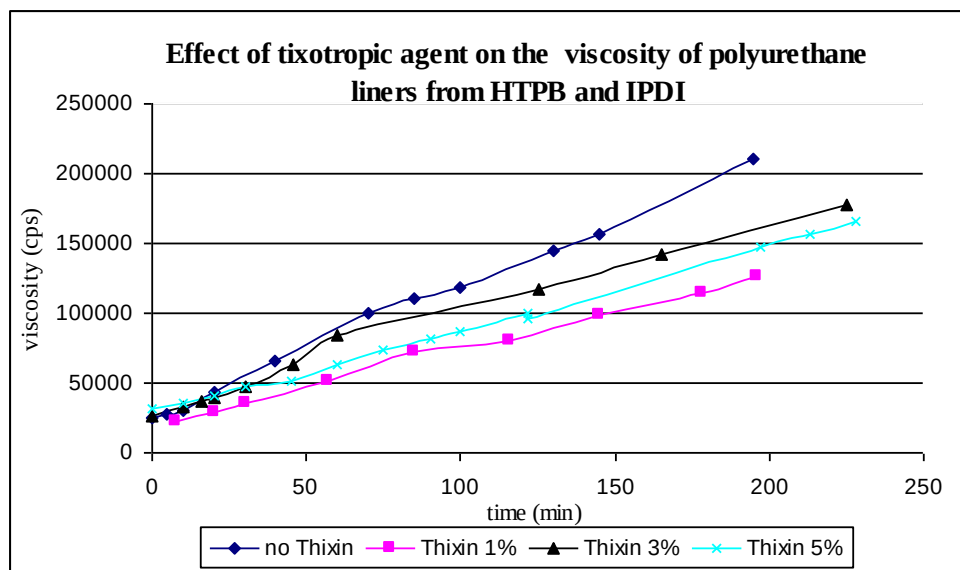


Figure 1: Viscosity curves (cure curves) of liners with 1, 3 and 5% of thixotropic agent Thixin R (NL Industries, U.S.).

3.2. Mechanical properties

Final mechanical properties in liners with Thixin R at 1, 3 and 5% were measured. Tensile strength and elongation at break were measured after curing at 20 °C for 7 days. Results are shown in Table 1:

Table 1: Final mechanical properties of liners after 7 days of curing at 20 °C.

Sample	Tensile strength (MPa)	Elongation to break (%)
IPDI 7,2%	0.53	440
1% Thixin R	0.58	255
3% Thixin R	0.51	412
5% Thixin R	0.54	350

3.3. Rheological properties of IPDI and TDI-cured liners

Firstly, a constant amplitude-frequency and a constant frequency-variable amplitude scan were made, necessary to set the amplitude and frequency sweeps to be used in time measurements. The parameters loss modulus (G'') and storage modulus (G') were obtained. In the scans, G'' is always greater than G' . This assures that liner formulations will flow if sprayed onto the inner surface of a rocket case before propellant is casted into.

Loss (G'') and storage (G') modulus curves for the liners cured with 9% isophorone diisocyanate (IPDI) at three different temperatures (7, 25 and 60 °C) did not intersect during the tested period (120 minutes). In all cases G'' is greater than G' , indicating that the liner will flow under applied stresses and could be applied by spraying. It was observed that the curves 60 °C were closer than at 25 and 7 °C, respectively. This confirmed that to accelerate curing is desirable to use a higher temperature, without compromising flow in the case of being applied by spray (as G'' was always greater than G').

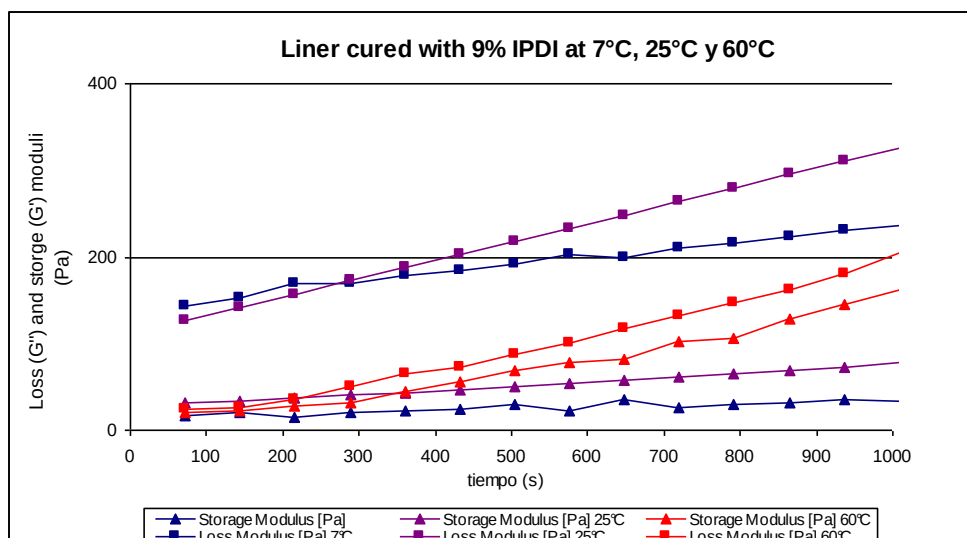


Figure 2: Storage (G') and loss (G'') moduli curves of HTPB-based liners cured with 9% isophorone diisocyanate (IPDI) at three different temperatures.

Other authors, while making a rheological study (DMA, dynamic mechanical analysis) found similar results but with a liner based on uncatalyzed HTPB cured with IPDI. They observed that G'' and G' curves intersected at 30 hours of curing. This is considered the time for the three-dimensional gel network to form (1). Beyond the gel time, liner would not flow.

In all cases, loss modulus increased during time, as viscosity increased as a results of the curing process. It was intriguing to observe that at 7 °C the complex viscosity curves were lower than at 25 °C. Indeed, this can be explained considering that two opposing effects are present: the temperature and the curing rate. When the temperature rises, the viscosity tends to decrease. Accordingly we would expect the viscosity at 7 °C to be greater than 25 °C. However, as the temperature increases, the rate of curing also increased and so did the viscosity. In our case, the effect of cure rate prevailed over the temperature effect, which have caused the viscosity at 25 °C to be greater than at 7 °C.

3.4. Liner formulation with TDI and TDI plus thixotropic agent

The same experiments were done with a liner formulation cured with TDI alone and with 1% of the thixotropic agent Thixin R at 7 and 25 °C.

In the frequency sweeps G'' curve was higher than G' curve at 7 °C but the behavior was the opposite at 25 °C. In the strain sweeps G'' curves were higher than G' curves at 7 °C and they intersected at 0.14% strain at 25 °C. These results suggested that the liner could be applied better at 25 °C. The results are shown in the following Figures:

When the thixotropic agent Thixin R was added at 1% (w/w), in the frequency sweeps G'' curve intersected G' curve at 15 1/s at 7 °C and at 65 1/s at 25 °C. In the strain sweeps G'' curves intersected G' curves at 0.14% at 7 °C and at 3% strain at 25 °C.

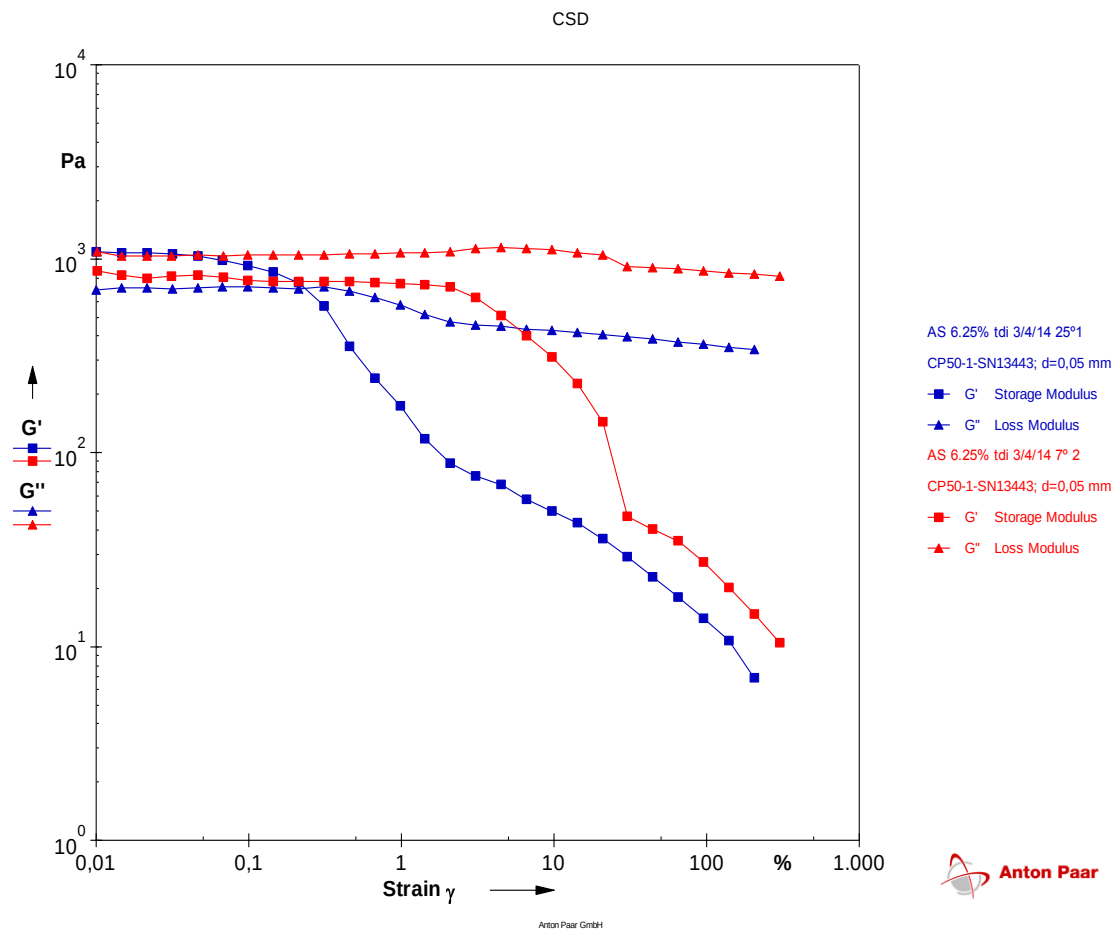


Figure 3: Storage (G') and loss (G'') moduli curves of liners with TDI vs. strain.

There are two opposite effects influencing curing: temperature and reaction rate. Increasing temperature has a pronounced effect on curing, accelerating crosslinking and the formation of a gel network. At the same time, increasing temperature diminishes viscosity. However, reaction rate overcame temperature effect, and curing was accelerated at 25 °C. The point of fluence (where G' and G'' intersects) was achieved at 25 °C but not at 7 °C. On the other side, when Thixin R was added, the fluence point was not altered at 25 °C, but was found at around 2% strain at 7 °C, while it was not found without Thixin R), as can be seen in the following Figure:

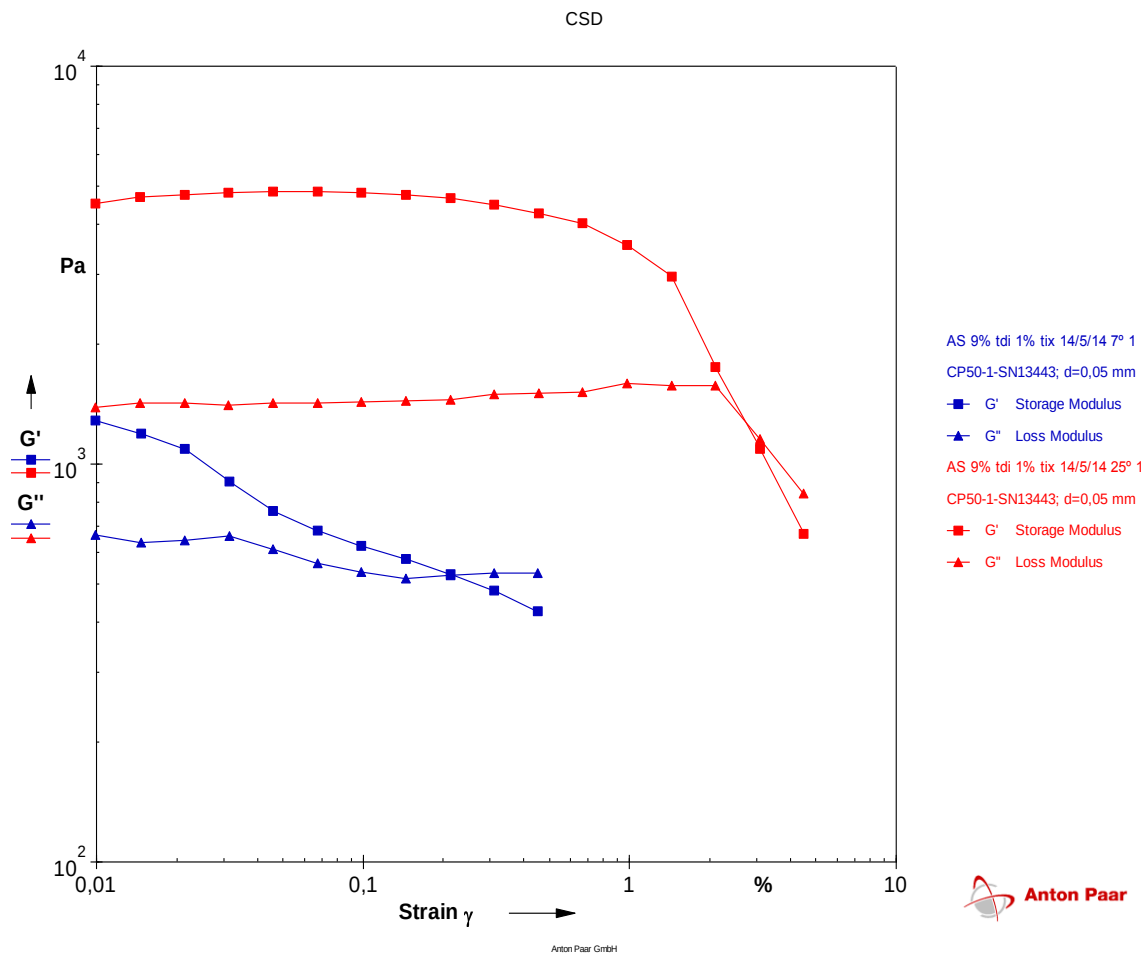


Figure 4: Storage (G') and loss (G'') moduli curves of liners with TDI and 1% of thixotropic agent Thixin R (NL Industries, U.S.) vs. strain.

4. Conclusions

TDI cured mixtures proved to be of practical value in our technological application as liner for composite propellants. However, IPDI-cured mixtures showed more advantageous as pot life is much smaller, allowing enough time for pilot plant and production operations. Utilizing this last system at low temperatures (7 °C) resulted in lower values of both loss and storage moduli (100 to 1000 Pa) than for TDI-cured mixtures, suggesting that application by aspersion will be facilitated. The addition of thixotropic additive lead to much lower viscosity values, without altering final mechanical properties. These results suggested that modification of liner mixtures with this additive could help application of liners without detrimental effect on liner performance.

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Fabrication and Characterization of ZnO Nanorods/Pd-Au Contacts

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ABSTRACT. Vertically aligned ZnO nanorods were grown with two-layer structure including a buffer layer of AZO (150-nm). RF sputtering method was used to grow ZnO nanorods on pre-deposited AZO buffer layer by thermal evaporation method. The XRD results confirmed the polycrystalline nature of the sample. The average height of 618-nm and the diameter of 474-nm of ZnO nanorods were measured with the SEM. The optical bandgap of the sample of 3.35 eV was estimated by Ellipsometric measurement. Shadow mask technique was used to deposit Au/Pd dots on the tip of the ZnO nanorods. The current-voltage (I-V) characteristics reveal the rectifying behavior of the contact with rectification ratio and ideality factor of 2534 at ± 5 V and 4.53 respectively.

Keywords: ZnO nanorods, RF sputtering, X-ray diffractometer, Atomic Force Microscopy, Scanning Electron Microscopy and Bandgap.

1. INTRODUCTION

Zinc Oxide (ZnO) has drawn enormous attention due to their fascinating optical, electrical, magnetic and chemical properties. The interest in ZnO semiconductor has increased in view of its direct wide bandgap of 3.37 eV and a large excitation binding energy (60 meV) [1]. It is the most promising oxide semiconductor having a variety of applications in transparent electronics, ultraviolet (UV) light emitters, chemical sensors, spin electronics, piezoelectronics and biomedical applications [2]. ZnO has a high value of electromechanical coupling through the c-direction making it suitable for widespread use in acoustic wave devices. One of the major advantages of ZnO is its stable wurtzite structure with lattice spacing $a = 0.325$ -nm and $c = 0.521$ -nm [3, 4]. This feature makes it an interesting nanomaterial. As a result, a diverse group of ZnO nanostructures could be grown in the past; these include nanowires, nanotubes, nanorings and nano-tetrapods [5]. ZnO nanorods (NRs) are extremely attractive due to their large charge carrier transport properties and great crystalline quality. ZnO nanostructures aid to electrical transport, UV emission, gas sensing and ferromagnetic doping. Vertical aligned ZnO nanorods caught attention because

of potential applications in field emitter, photonics, vertical transistor and UV laser. ZnO nanorods are easy to grow and can produce high quality of p-n heterojunctions on any p-type substrate. The lattice matching epitaxial between ZnO and the supporting substrate determines the quality of vertical alignment and surface area to volume ratio. The detection sensitivity of ZnO nanorods based FET biosensors is increased due to large surface area to volume ratio of ZnO nanorods. There are several methods including chemical vapor deposition, pulsed laser deposition (PLD) [6, 7, 8, 9], spray pyrolysis methods [10], hydrothermal methods [11, 12], sol-gel solution method [9], thermal evaporation [13], RF/DC sputtering [14, 15, 16] and activated-reactive evaporation [17] etc for the preparation of oriented ZnO nanostructures.

In this paper, the thermal evaporation and RF-sputtering method have been opted to obtain high quality ZnO nanorods. The properties of ZnO nanorods deposited by the two-step approach are dependent on the deposition parameters such as a substrate material, substrate temperature and distance from the substrate to source. In order to form metallic contacts Gold/Palladium (Au/Pd) (80:20) dots have been evaporated on the top of the vertically aligned NRs [18]. In the present studies, ZnO nanorods synthesis and characterization have been done. The structural, morphological, crystalline orientations, optical and electrical properties of ZnO NRs grown by the above method are studied.

2. EXPERIMENTAL DETAILS

2.1. Preparation of ZnO Buffer Layer

Before growing of ZnO nanorods, a buffer layer [19] was formed on the p-type (100) silicon (Si) substrate with size of 10mm x 5mm x 0.5mm. Prior to use, the Si substrate was cleaned by RCA (the Radio Corporation of America) method [20] to remove contaminations and loaded to the substrate holder. A 50-nm ultra-thin Al-doped ZnO (1% Al) (AZO) [21, 22, 23] buffer layer was deposited onto Si substrate using thermal evaporation setup unit (Hind High Vacuum coating unit, Model: 12A4D), the AZO buffer layer is required to improve the density, vertical alignment and the orientation of growth of ZnO nanorods. The heating filament was a conventional tungsten filament in which material was kept. The distance between the substrate and source was adjusted to 140 mm. For 1% AZO buffer layer, 5 gm of ZnO powder (highly pure ZnO (99.99% from Alfa Aesar) and 0.0313 gm of Al_2O_3 (highly pure Al_2O_3 (99.999% from Alfa Aesar)) powder) have been taken. Then the mixture was thoroughly mixed with polyvinyl alcohol (PVA) for about 2 hr manually with the help of agate mortar and pestle sets. AZO pellet of 10-mm diameter was prepared. The base pressure was 10^{-6} mbar of the vacuum chamber. The substrate was kept at room temperature during the deposition of the films. The thickness of AZO buffer layer was set at 50-nm for digital thickness monitor attached to thermal evaporation setup unit. In order to improve the quality of AZO buffer layer for the growth of ZnO nanorods, the sample was subjected to annealing at 773 K in hot muffle furnace for 1hr [24]. Then the sample was taken out for the next deposition after the film was cooled down to room temperature.

2.2. Preparation of ZnO nanorods

After the formation of AZO buffer layer [16], ZnO nanorods were grown by using RF-sputtering. ZnO (99.99% pure) target of 3 mm thickness and 50.8-mm diameter was prepared with the help of a hydraulic press and kept in a furnace at 1073 K for 5 hr. The sample was placed on the sample holder fixed at distance of 100-mm from the source. The vacuum chamber was evacuated to $\sim 10^{-6}$ mbar before sputtering. In order to have high-deposition rate, RF power was kept 300W while sputtering at room temperature. The flow rate of argon gas and oxygen gas in the chamber was controlled by Mass flow controller (MFC1 and MFC2). Highly pure Oxygen and Argon gas were used for the growth of ZnO nanorods in the chamber with Ar:O₂ ratio set at 80:20 sccm. The digital thickness monitor displayed the rate of deposition and thickness. The deposition time was set at 1hr, so the thickness of the deposited films was approximately 600-nm.

Preparation of Schottky and ohmic contacts

The Gold/Palladium (Au/Pd) dots have been evaporated on the top of the vertically aligned ZnO nanorods using shadow mask technique to form Schottky contacts. This process was done by using Sputter Coater unit. The Schottky contact area was $\sim 7.85 \times 10^{-3} \text{ cm}^2$. Aluminium was deposited at the backside of Si using thermal evaporation unit to provide ohmic contact to the device.

3. RESULTS and DISCUSSION

3.1. Structural Analysis

The crystalline nature and structural properties of the as-grown ZnO nanorods were studied by using X-ray diffractometer (XRD) [Rigaku Smartlab, with Cu-K α radiation ($\lambda=1.540568 \text{ \AA}$)]. Fig.1 shows the XRD diffraction pattern of the ZnO nanorods. These samples prepared by rf-sputtering were pre-annealed at 773 K. The XRD diffraction peaks were found at 34.29° and 62.77° corresponding to (002) and (103) planes in the ZnO nanorods respectively. The deposited film has a random polycrystalline nature in the z-direction. The quality of ZnO nanorods, as well as crystalline nature of the sample was found to improve following pre-annealing temperature at 773 K (not shown here). The crystallite size (D) of the ZnO nanorods was obtained from the Debye-Scherrer equation (1) [25]:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where β is the full-width at half maximum (FWHM) and peaks are located towards an angle 2θ . All the parameters are listed in Table I. The strain in the ZnO nanorods was obtained by the equation (2) [23]:

$$\xi = \left[\frac{\lambda}{D \cos\theta} - \beta \right] \times \frac{1}{\tan\theta} \quad (2)$$

Table-I Structural Parameters of ZnO nanorods deposited on Si Substrate

2θ (°)	FWHM (°)	Crystallite Size (Å)	Interplanar Spacing (Å)	Strain
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34.297	0.437	190.39	2.614	2.747×10^{-3}
62.77	0.99	94.07	1.4802	3.147×10^{-3}

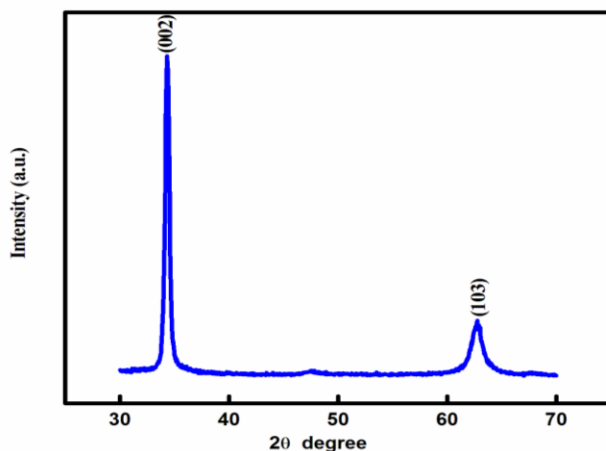


Figure 1 XRD Image of ZnO nanorods

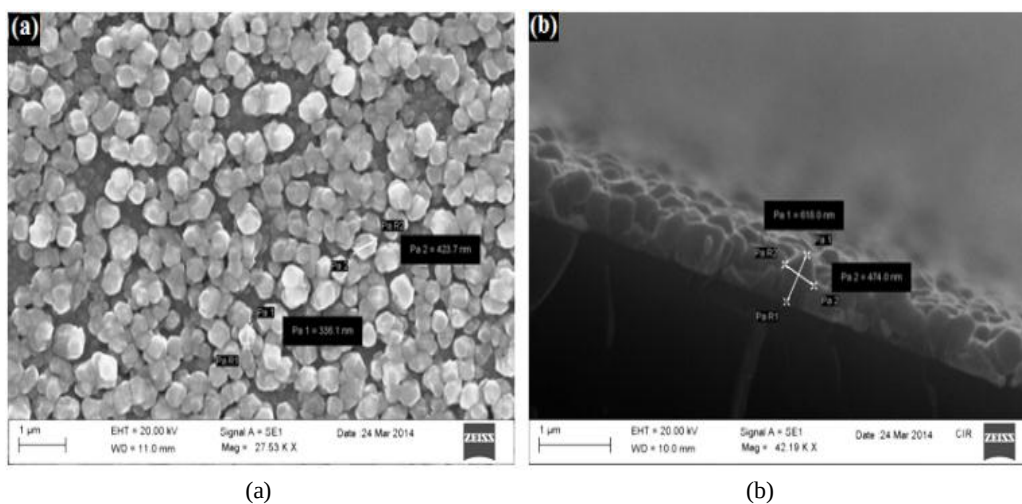


Figure 2 SEM Images of ZnO nanorods on Si substrate (a) Top view and (b) Cross-sectional view

3.2. Surface Morphological Analysis

The surface topography and size of the sample of nanorods were characterized using a scanning electron microscope (ZEISS EVO MA 15). Fig. 2(a) shows 2-D SEM image of the ZnO nanorods Fig. 2(b) shows a cross-sectional SEM image of the as-synthesized ZnO nanorods grown on a Si substrate. The typical average height of the nanorods was 618-nm and the diameter was of 474-nm.

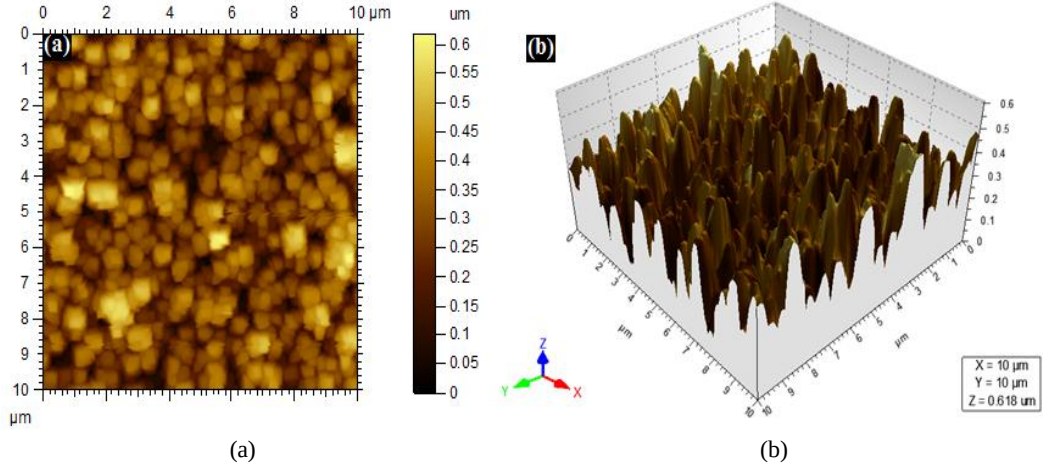


Figure 3 AFM Images of ZnO nanorods on Si substrate (a) 2-D and (b) 3-D

3.3. Surface Topographical Analysis

The roughness and topography of the ZnO nanorods were evaluated by using Agilent 5500 Atomic Force microscopy (AFM). The AFM images are shown in Fig.3. The grain size, average roughness (R_a), root mean square (rms) roughness (R_q) and total roughness (R_t) of the ZnO nanorods were also calculated from AFM results using picoimage software. All the parameters are listed in Table II.

Table-II Parameters obtained by AFM studies of ZnO nanorods

Grain Size (nm)	R_a (nm)	R_q (nm)	R_t (nm)
247	48	62.7	35.6

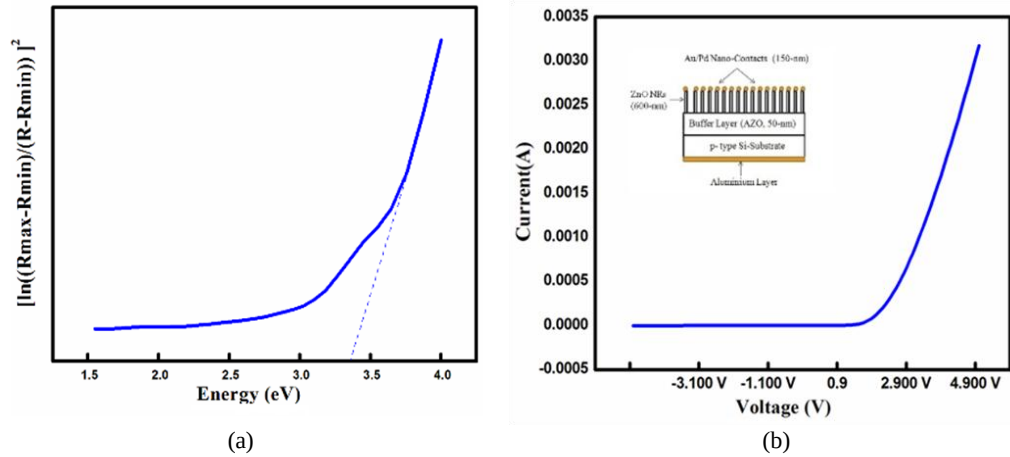


Figure 4 (a) Energy bandgap of ZnO nanorods on Si substrate (b) I-V Characteristics of the device

3.4. Optoelectronics Analysis

The thickness and optical bandgap of ZnO nanorods were determined by using ellipsometric measurements (J.A.WOOLLAM Co. Inc. (model VB-400)). The thickness was measured to be of the order of 600-nm and the optical bandgap was calculated to be 3.35 eV shown in Fig. 4(a). The optical bandgap was calculated by using equation (3) given by [26]:

$$2\alpha t = \ln\left(\frac{(R_{max}-R_{min})}{(R-R_{min})}\right) \quad (3)$$

where R is the reflectance, α is the attenuation constant and t is the film thickness.

Table-III Parameters obtained by I-V Characteristics using Semiconductor Device Analyzer

Parameters	Experimental Data
Barrier Height(ϕ_B)	0.96 eV
Ideality Factor(η)	4.53
Rectification Ratio	2534

3.5. Electrical Analysis

I-V characteristics for the Au/Pd/ZnO/Si contact were measured using Semiconductor Device Analyzer (B1500A) by placing the samples on the probe station. The device structure is shown as an inset in Fig.4(b) which depicts the measured forward and reverse I-V Characteristics at room temperature. The device is forward biased by connecting the positive terminal of the supply to the metal contact and the negative terminal to the ZnO nanorods. For reverse bias case the polarities are interchanged. Rectification characteristics are obtained for the device with a rectification ratio of 2534 at ± 5 V. The current across a Schottky diode, the barrier height (ϕ_B) and ideality factor (η) have been calculated using by thermionic emission theory.

$$I_0 = AA^*T^2 e^{-q\phi/kT} \quad (4)$$

$$I = I_0(e^{qV/\eta kT} - 1) \quad (5)$$

where η is the ideality factor, k Boltzmann constant, and T is the absolute temperature. A is the Schottky contact area, A^* the effective Richardson constant (theoretically $A^*=32 \times 10^4 \text{ Am}^{-2} \text{ K}^{-2}$) and ϕ_B is the barrier height.

The reverse saturation current (I_0) and the ideality factor (η) were extracted from the measured I-V characteristics.

4. CONCLUSION

ZnO nanorods were successfully grown on p-silicon (100) substrate containing a pre-deposited buffer layer of AZO with the help of RF sputtering method. XRD, SEM, AFM and Ellipsometer were used to study the structural, morphological, topographical and optical properties of ZnO nanorods. The ZnO

nanorods grown over the buffer layer have large crystallite size, small FWHM and less strain. The surface morphology study by SEM confirms the growth of ZnO nanorods. The topography of the surface shows that the nanorods grown was symmetrical and vertically aligned. The grain size and the roughness of the surface were also studied. The optical bandgap for the ZnO nanorods was measured to be 3.35 eV. The I-V characteristics reveal that the device has a rectifying behavior with a rectification ratio and ideality factor of ~2534 and 4.53 respectively.

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Salt-Assisted Self-Propagating High-Temperature Synthesis of Aluminium Nitride Powders

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Abstract: Powders of aluminum nitride can be prepared by self-propagating high-temperature synthesis (SHS) between aluminum and nitrogen but its high exothermic effect causes melting and evaporation of aluminum and low efficiency of such a reaction. The presence of inorganic salt in the starting powder mixture can decrease heat evolved in the SHS reaction, hinders melting and coalescence of aluminum, and facilitates penetration of nitrogen into the interior of a powder bed. Mixtures of alumina powders with different grain sizes and different amounts of aluminum nitrate were subjected to the SHS reaction under 0.1 or 1 MPa nitrogen. The powders were composed of aluminum nitride, unreacted aluminum, aluminum oxynitride and, in some cases, corundum. The final effects depend strongly on the amount of introduced salt, aluminum powder morphology and, to a lesser extent, on a nitrogen pressure.

Keywords: Aluminium Nitride, Self-Propagating High-Temperature Synthesis, Salt Assisted Synthesis

1. Introduction

Aluminum nitride is a promising functional ceramic material due to its high thermal conductivity ($319 \text{ W m}^{-1} \text{ K}^{-1}$ for a single crystal and about $200 \text{ W m}^{-1} \text{ K}^{-1}$ for polycrystalline materials) and to low electrical conductivity associated with a relatively wide band gap, 6.2 eV [1-3]. Sintered, dense aluminum nitride materials are also characterized by good mechanical properties: flexural strength of about 400 MPa and hardness of about 15 GPa [4]. They are used for example in electronics as substrates for integrated circuits instead of toxic beryllium oxide for better heat dissipation.

There are many methods of preparing aluminum nitride powders. The thermal treatment of aluminum powder in a nitrogen or ammonia atmosphere at elevated temperature for several hours is a commonly used method [5]. A carbothermal reduction with simultaneous nitriding of aluminum oxide at 1800 °C can be also used but the product is contaminated with carbon and highly aggregated [6].

Similarly, the aluminum oxide reduction may be carried in the flow of ammonia at 1250 °C for 5h [7]. When the reaction in a gas phase is used, aluminum chloride is reacted at elevated temperature with ammonia and nitrogen as a carrier gas but the substrate is hygroscopic and the product is often contaminated with ammonium chloride [8]. Aluminum nitride powders can also be prepared in an electric arc, but the apparatus, control conditions and energy consumption are considerable obstacles [9].

The self-propagating high-temperature synthesis (SHS) is a relatively simple and quick method of aluminum nitride preparation. In such a case, the reaction between aluminum powder, usually in a form of porous and loose bed, and nitrogen is initiated. Very high heat of the reaction causes the increase of temperature high enough to melt and partially evaporate of aluminum which is the reason of relatively low efficiency of the process. Two ways are usually used to avoid such drawbacks – the decrease of a nitrogen partial pressure and dilution of the aluminum bed with aluminum nitride powder.

There are several papers describing the SHS synthesis of aluminum nitride powders where a small amount of inorganic substances are added. Ammonium chloride added to aluminum powders with different grain size was one of the used additives [10]. It was stated that the optimum amount of salt depended on the aluminum grain size; the larger aluminum grains the highest salt content. Ammonium fluoride played similar role [11, 12]. Efficiency of the SHS synthesis from mixture of the aluminum and aluminum nitride powders increased when a small amount, from 0.5 to 1.5 mas%, of NH_4F was added. In another experiment, carbon soot in the proportion to aluminum powder up to 1.75 was used as an additive [13]. The highest yield of the SHS reaction was reached for carbon to aluminum ratio of 1.25 and when the reaction was performed under nitrogen pressure of 0.5 MPa. The addition of Teflon, 0.015 mole, and copper, 0.1 mole, resulted in creation of elongated nanostructures of AlN [14].

The described influence of the presence of inorganic salts on the SHS synthesis of AlN is usually attributed to their reaction with surface of aluminum grains. Thermal decomposition of ammonium chloride or fluoride leads to formation of very reactive atomic nitrogen as well as an electronegative anions that react with aluminum oxide present on the surface of aluminum grains which facilitates its removing. In our opinion, the presence of a higher amount of inorganic salt in the starting powder mixture can also decrease heat evolved in the SHS reaction, hinders melting and coalescence of aluminum, and facilitates penetration of nitrogen into the bed interior. The aim of the paper was the SHS synthesis of aluminum nitride powders in the presence of ammonium nitrate using aluminum powders with different grain sizes and under different pressures of nitrogen.

2. Experimental

Two commercial aluminum powders (Benda-Lutz) were used in the preparation. The first one, marked as Al-7, was composed of rounded but irregular grains with average size about 8 μm . The

second powder with irregular and not so rounded grains of about 50 μm was marked as Al-63. Fig. 1 shows SEM pictures and grain size distribution of the alumina powders.

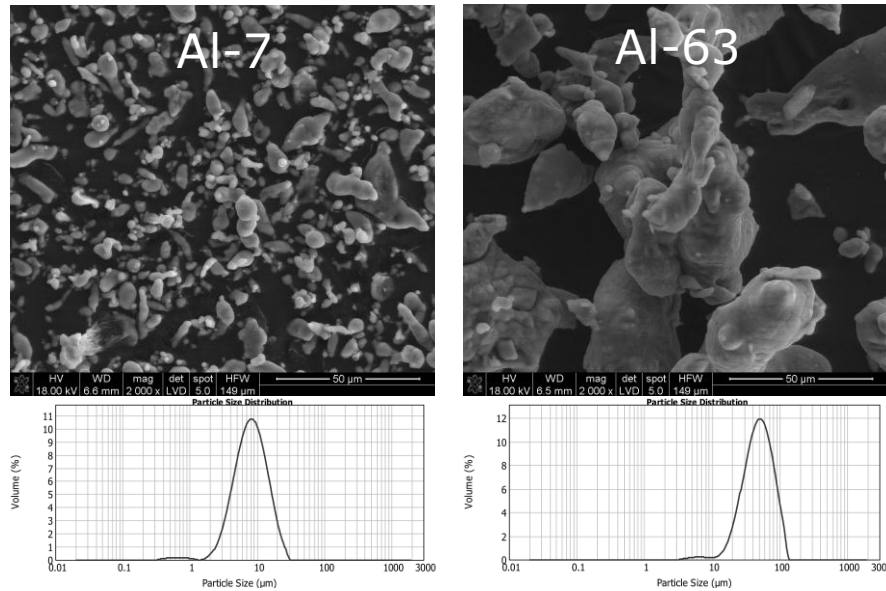


Fig. 1 SEM pictures and grain size distribution of the aluminum powders used in the preparation.

The alumina powders were mixed in a ball-mill with ammonium nitrate for 30 min using zirconia grinding media and small amount of dry isopropanol. The amounts of salt were 10, 20, 30 and 40 vol. %. The powder mixtures were dried at the room temperature and placed in a container made of graphite foil in the form of a loose, porous bed. The container was thermally isolated with corundum wool and put into a pressure chamber. The chamber was vacuumed and filled with nitrogen to 0.1 or 1 MPa pressure. The synthesis was initialized by a current flow through the graphite container for five minutes.

Phase composition of the powders was determined by the X-ray diffraction analysis and the Rietveld refinement was used to determine the quantitative phase content. The Empyrean diffractometer system (Panalytical) equipped with a copper lamp, Johansson monochromator ($\text{CuK}_{\alpha 1}$ radiation) and the X'Celerator strip detector was used. Morphology of the powders was observed by means of scanning electron microscopy (Nova NanoSEM 200, FEI).

3. Results and discussion

The X-ray diffraction analysis reveals that all SHS-derived powders are composed of aluminum nitride, aluminum, aluminum oxynitride with the spinel structure, γ -AlON, and corundum. Fig. 2 shows changes of aluminum nitride content in the SHS prepared powders.

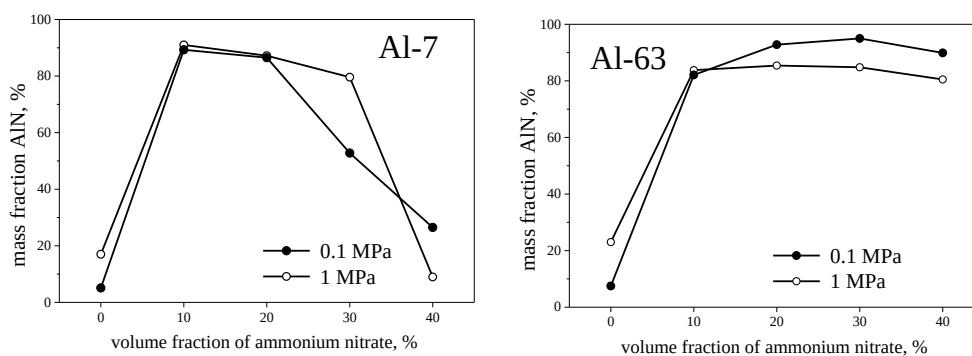


Fig. 2 Changes of mass fraction of aluminum nitride in the SHS-derived powders in relation to the salt content in the starting powder mixture.

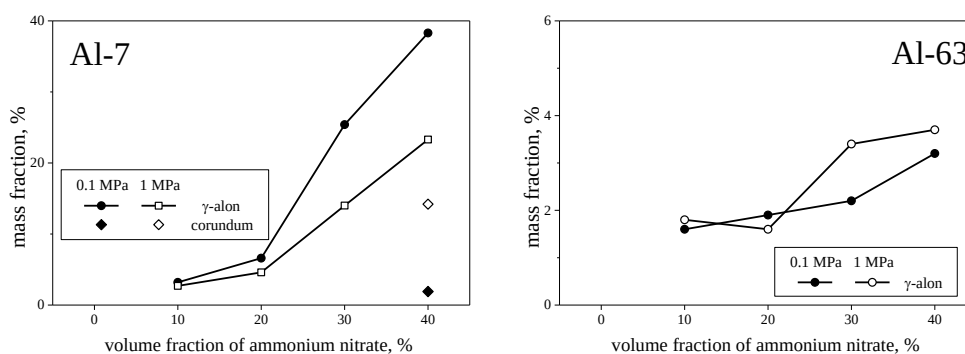


Fig. 3 Changes of mass fraction of the oxide phases in the SHS-derived powders in relation to the salt content in the starting powder mixture.

In the case of pure aluminum powder, the amount of aluminum nitride in the SHS-derived powder did not exceed 25 mass%. Contrary to expectations, higher amounts of AlN were observed in the powders synthesized at the higher pressures of nitrogen. The 10 mass% addition of salt led to a significant increase in efficiency of the AlN synthesis reaction. In the case of the Al-7 powder, regardless of the used pressure of nitrogen, after the SHS synthesis the powders contained over 90 mass% of aluminum nitride, while for the Al-63 powder it was over 80 mass%. The effect associated with a further increase of the amount of the salt varied depending on the alumina particle size. In the aluminum powder with the smaller grains, Al-7, the increase of ammonium nitrate content in the starting powder mixture led to a decrease of the amount of AlN in the powder after the SHS reaction. This decrease was so large that the powder obtained from a mixture containing 40 vol.% AlN amount of ammonium nitrate is less than 30 mass%. The nature of the presented relations show also that the nitrogen pressure has a little effect on the amount of the resulting AlN. In the powder with the larger grains, Al-63, and the lower nitrogen pressure, 0.1 MPa, an increase of the amount of salt initially led to a small increase in the content of AlN, reaching a maximum for 30 vol.% NH_4NO_3 (95 mass% AlN),

and then decreased slightly. In the case of the higher nitrogen pressure, 1 MPa, a slight decrease of the AlN content in the SHS-derived powders was already visible in the starting powder mixture with 20 vol.% ammonium nitrate.

Unreacted aluminum, aluminum oxynitride with spinel structure, γ -AlON, and corundum, in the case of Al-7 powder, were balance phases in the SHS-derived powders. Fig. 3 shows changes of the oxide phase contents in relation to the amount of salt in the starting mixtures. The presence of aluminum oxide in the powders results from a reaction between aluminum and oxygen, or nitrogen oxides resulting from the ammonium nitrate decomposition. According to the previous work, it can be assumed that aluminum oxynitride is formed in the secondary reaction between aluminum nitride and aluminum oxide [15]. This reaction is endothermic and high temperature is required for its occurrence, therefore it can be assumed that a higher specific surface of the Al-7 powder leads to a more intensive course of the highly exothermic reaction between aluminum and nitrogen, and consequently to a higher temperature. A higher amount of salt (thus a higher amount of oxygen in the system) also intensifies this reaction.

SEM observations reveal that morphology of the SHS-derived powders is complex and very diversified. Fig. 4 shows some SEM pictures of the SHS-derived powders prepared, from different aluminum powders under different nitrogen pressure and with different amounts of salt. The first three pictures, Fig. 4.a-c, present the morphology of the powders prepared without the presence of salt. Most of the aluminum nitride grains have regular isometric shapes and sizes from 5 to 10 μm . The formation of such particles takes place on a surface of the aluminum grains; the AlN grains visible in Fig. 4.b are located at grain boundaries of the metal. Poreless aluminum polycrystals suggest that they are a result of a liquid metal solidification. Plate-like or elongated AlN grains, suggesting the VLS (vapour-liquid-solid) or the VS (vapour-solid) mechanism of their formation, indicate the presence of gas and/or liquid aluminum during the SHS reaction, Fig. 4.c.

A similar diversity of morphology can be observed in the powders synthesized by the SHS method with the addition of ammonium nitrate; Fig. 4.d-i presents SEM images of the selected powders. Most of the aluminum nitride particles have regular shapes and sizes up to 1 μm , Fig. 4.d and Fig. 4.e. High temperature of the synthesis makes these grains form aggregates and agglomerates larger than hundreds of microns. Also in this case plate-like and elongated grains are visible (Fig 4.f and 4.g), indicating the presence of liquid and gaseous aluminum. Both whiskers and forms of larger diameter composed of a single, hexagonal plates of nanometer sizes can be recognized among elongated crystals of AlN. It is possible to find some areas showing a sequential proceeding of reactions. Fig. 4.h presents the aggregate composed of aluminum nitride grains coated with short needle-like crystals of the same phase. In the case of the powders synthesized in the presence of larger amounts of salt very large and poreless aggregates can be observed, Fig. 4.i. On their surfaces individual, smaller particles of AlN are placed probably due to the secondary reaction of liquid aluminum with nitrogen. Large,

well-formed grains are aluminum oxide the occurrence of which must also be related to the presence of liquid aluminum and/or aluminum oxide.

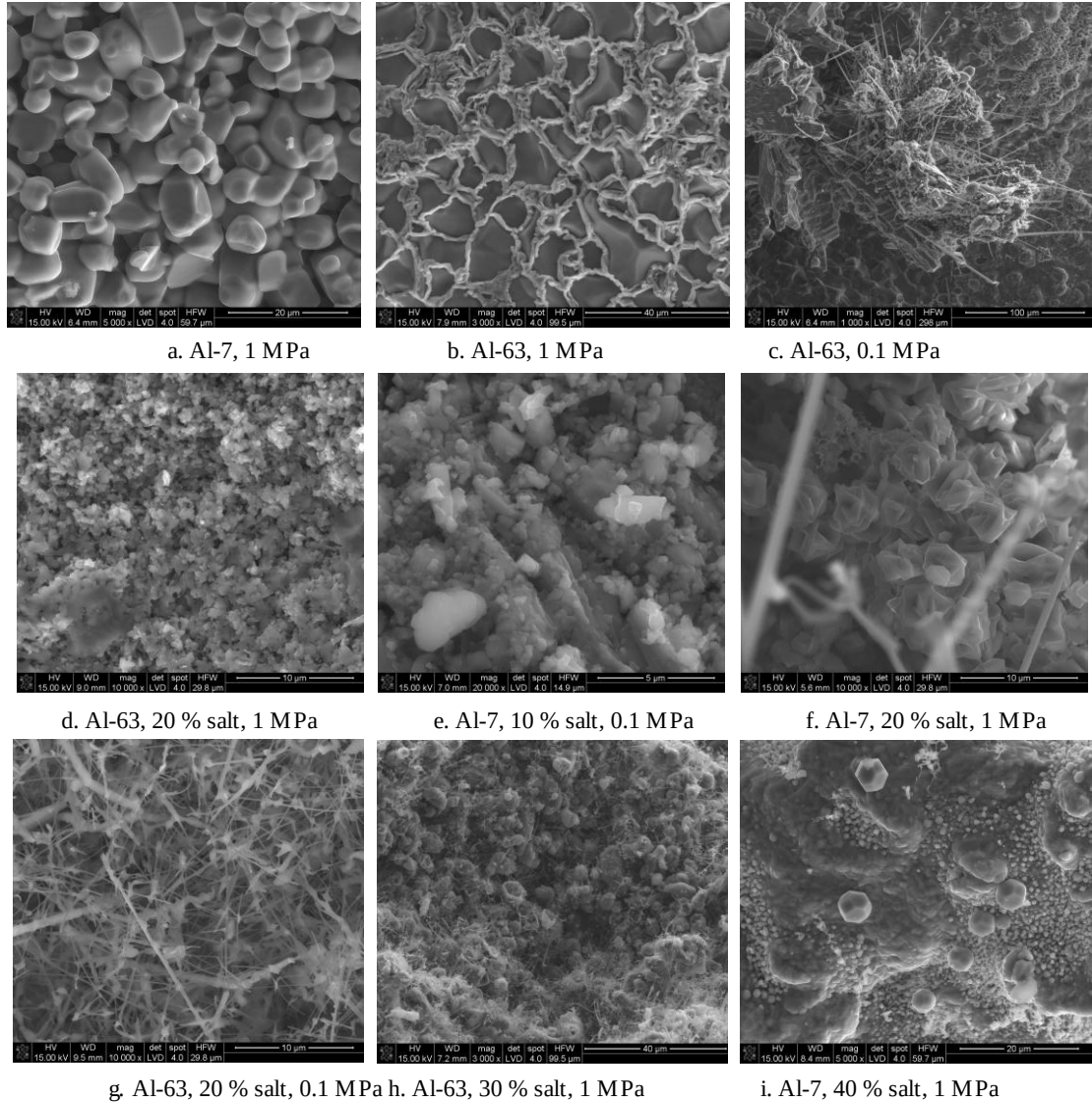


Fig. 4 SEM images of the SHS-derived powders.

4. Conclusions

Aluminum nitride can be prepared by a direct reaction between aluminum and nitrogen although the high heat of this reaction required the application of low nitrogen pressure and/or dilution of aluminum powder with AlN. The presented results show clearly that the presence of ammonium nitrate in the starting powder mixture for the SHS synthesis significantly improves efficiency of this

reaction. The effects depend strongly on the amount of introduced salt, aluminum powder morphology and, to a lesser extent, on a nitrogen pressure. The larger are the aluminum grains the larger is optimal amount of ammonium nitrate, which gives over 90 mass% of aluminum nitride in the final powder. The prepared powders were characterized by a complex morphology; besides isometric AlN grains, plate-like and elongated particles can be seen, which indicates the presence of gaseous and/or liquid phases during the reaction.

Acknowledgements

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Poly (Acrylamide-co-Acrylic Acid) Hydrogels Containing TiO₂ Nanoparticles for Antimicrobial Applications

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Summary: Temperature and pH responsive poly(acrylic acid -co- acrylamide) hydrogels containing three different ceramic filler concentrations, namely poly(AA-co-AAm)-TiO₂(x), (x = 3, 5, 10%), were successfully synthesized and characterized.

Acrylic acid (AA) and acrylamide (AAm), was copolymerized at different ratios, (1/0, 3/2, 1/1, 2/3 and 0/1), using potassium persulphate initiation system in presence of a crosslinking agent and appropriate doses of TiO₂, to yield hydrogels. The X-ray diffraction patterns confirmed the presence of well dispersed anatase TiO₂ nanoparticles with tetragonal body centered structure. Size and distribution of the nanoparticles and their dependence on the dose of TiO₂ were considered using the scanning electron microscopy (SEM). The chemical structure of the hydrogels was determined by ATR-FTIR spectroscopy. Swelling capacity and kinetics of swelling of the obtained hydrogels were studied and their corresponding swelling behavior was followed at pH 4, 7 and 8 in buffered solution at 310 K. Results showed that swelling performance is rather sensitive to the pH of the media. Specific polar interactions of the carboxylic groups of the hydrophilic acrylic acid component with the surface of TiO₂ particles modulate the behavior of the composites against the hydration processes at different pH. Furthermore the antimicrobial activities of the hydrogels were reported. Subsequently the hydrophilic and biocompatible proprieties of these hydrogels make them suitable for pharmaceutical applications essentially as drug targeting matrix, since TiO₂ nanoparticles are largely used as excipient in different drug formulation.

Keywords: hydrogel nanocomposite, TiO₂-feller, swelling behavior, kinetic study, antimicrobial activity.

1. Introduction

Recently polymer matrix–ceramic filler composites receive increased attention due to their interesting optical, electrical and electronic properties ^[1-3]. Incorporation of inorganic nanoparticles into polymer matrix can significantly affect the characteristics of the matrix. The obtained composite might exhibit improved thermal, mechanical or optical ability. Subsequently the properties of polymer composites depend on the incorporation manner of the nanoparticles, their size, shape, concentration and the nature of their interaction with the polymer matrix. Additively hydrogels have been used to maximize the efficiency of decontamination of toxic organic compounds. Using their swelling ability they can absorb toxic organic compounds. Thus, rapid decontamination of toxic organic compounds is possible, allowing quick treatment of polluted water ^[4-5]. Titanium dioxide has been the subject of many studies for the reason that it is inexpensive, non toxic at low concentration and it can exist in three distinct structures, which are known as rutile, anatase and brookite ^[6].

Syntheses of poly(acrylic acid-co-acryl amide) (PAA-co-AAm) hydrogels, containing 0.67, 1.00, 1.25, 1.50 wt % of AAM were previously synthesized by Katime and al. and release behaviour of theophylline from these hydrogels were widely discussed [7].

In this study, hydrogel-TiO₂ nanocomposites have been synthesized, (using the anatase crystalline phase of TiO₂ nanoparticles), by a methodology, which involves formation of TiO₂ nanoparticles within swollen poly(acrylamide-co-acrylic acid) hydrogels. So the poly(acrylic acid-co-acryl amide) hydrogels containing 0%; 34%; 50%; 66% and 100% wt % of AAM using simultaneously 3% ; 5% and 10% of TiO₂ nanoparticles were synthesized. Then we studied swelling behaviour of poly(acrylic acid-co-acryl amide)-TiO₂ (3%) hydrogels at (1/1) ratio in different pH media. Results will show that the introduction of small amount of TiO₂ nanoparticles into polymer matrix is sufficient to modify the polymer matrix and make important change in the polymer structure, involving new properties in the initial material.

2. Experimental

2.1. Materials

The two monomers used in this study, namely acrylic acid (AA) (Fluka, HPLC grade) and acrylamide (AAm) (Merck, HPLC grade) and the crosslinking agent N,N-methylene-bis-acrylamide (MBA) (Fluka, HPLC grade), were used as received. Titanium dioxide, TiO₂ powder with the diameter average of 4.5nm (Sigma-Aldrich) belongs to anatase structure and potassium persulphate (KPS) provided by (Fluka), was used as initiation system. In the other hand standard bacterial cultures, were supplied by Pasteur Institute (Delly Brahim), Algiers, thus double distilled water, was used throughout the investigations.

2.2. Synthesis of poly(acrylamide-co-acrylic acid) hydrogels

Hydrogel matrix-ceramic TiO₂ nanocomposites were prepared in three different concentrations. Acrylamide was copolymerized with acrylic acid at different ratios in presence of desired amount of TiO₂ (3%, 5% and 10%), using potassium persulphate initiation system and a crosslinking agent, N,N-methylene-bis-acrylamide, MBA. The solution was out gassed with gaseous nitrogen in glass test tubes. Polymerization was carried out at a temperature of 323 K for 24 h. The resultant crosslinked polymer rods, were immersed in water for one week to remove any possible residual monomers. Discs were obtained from the hydrogel rods by cutting with a lathe. Then they were dried at ambient temperature for several days at 313 K, until constant weight.

2.3. Characterization of hydrogel-TiO₂ nanocomposite sample

A JSM-6300 scanning electron microscope (SEM) (JEOL Ltd., Japan) was used to investigate the surface morphology of the hydrogel/TiO₂ composite sample after (Au) coating. The anatase structure of TiO₂ was studied using X-ray diffraction (XRD). The (XRD) patterns of the samples were recorded on a Rigaku (D/MAX-2200 Ultima/PC) diffractometer with Cu K α radiation and the samples were analyzed from 5° to 80° (2 θ). Hydrogels-TiO₂ nano-composites were characterized by Fourier transform infrared (FTIR) spectroscopy, on a universal attenuated total reflectance (ATR) Spectrum-one Perkin-Elmer spectrophotometer. The spectra were recorded at room temperature from 650 to

4000 cm^{-1} , with a resolution of 2 cm^{-1} . A background spectrum without any sample was subtracted from all spectra. The prepared hydrogel samples were screened in vitro for their antimicrobial activities against bacterial and fungal micro-organisms.

2.4. Swelling experiments

Dynamic swelling experiments were performed by placing the glassy discs in a double distilled water bath at 310 ± 0.2 K and measuring their weight gain as a function of time. The disk were extracted from the bath at different times, dried with filter paper and then weighed in a Mettler AE 200 balance. The degree of swelling, W_t , is expressed as the percentage of water in hydrogel at any instant during swelling:

$$W_t(\%) = (\text{weight of swollen disc} - \text{weight of dry disc}) / (\text{weight of swollen disc}) \quad (1)$$

Swelling behavior was examined for the hydrogels poly(AA-co-AAm)-TiO₂ (3%), in different ratios (1/0, 3/2, 1/1, 2/3, and 0/1), the experiments were performed twice and the data reported are mean values, hence the antimicrobial activity was examined for the hydrogels poly(AA-co-AAm)-TiO₂ (3, 5 and 10%) in the (1/1) ratio.

3. Results and discussion

3.1. Morphology study

Scanning electron spectroscopy, SEM, provided very useful information about the particle size, polydispersity profile and location of ceramic fillers inside and outside of the material. Figure 1, shows polydisperse repartition of TiO₂ nanoparticles and also presence of agglomeration on the surface of the hydrogels. As it can be seen the number of the particles increased with increasing TiO₂ nanoparticles concentration .from 3 to 10%.

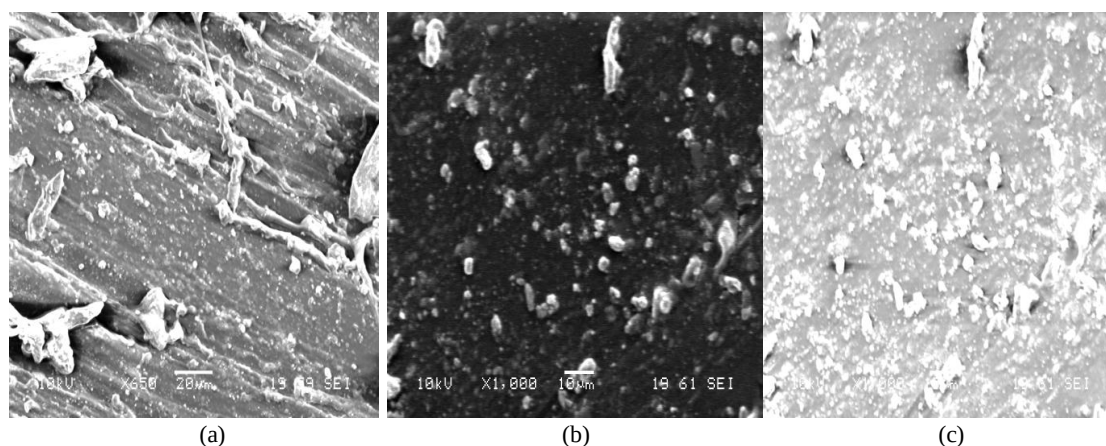


Figure 1. SEM image of poly(AA-co-AAm)-TiO₂ (x) (1/1), hydrogel with (a) x = 3%, (b) x = 5% and (c) x = 10% of TiO₂.

3.2. X-ray diffraction study of the hydrogel

Figure 2, gives the X-ray diffraction (XDR) patterns of the doped ceramic fillers hydrogels, poly(AA-co-AAm)-TiO₂ (3%) in (1/0, 3/2, 1/1, 2/3, and 0/1) ratios. The peaks exhibited at 2θ values 27.13°, 35.83°, 38.33°, 44.67° and 54.34° are in good agreement with those corresponding to the tetragonal centered body anatase structure of TiO₂ (25.36°, 37.85°, 38.64°, 48.15° and 53.97°) as reported by ASTM data and assigned to reflections through to the positions (101), (103), (004), (200) and (105) respectively. This result constitutes a proof of the presence of nano-sized TiO₂ particles in the analyzed hydrogels, additionally to the agglomerated particles seen by SEM analyses.

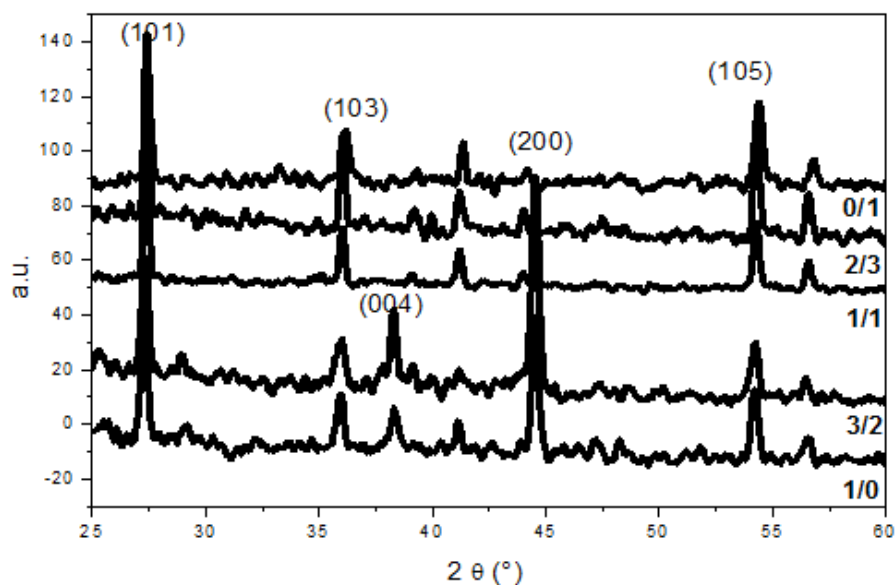


Figure 2. X-ray patterns of poly(AA-co-AAm)-TiO₂ (3%) hydrogels at different ratios.

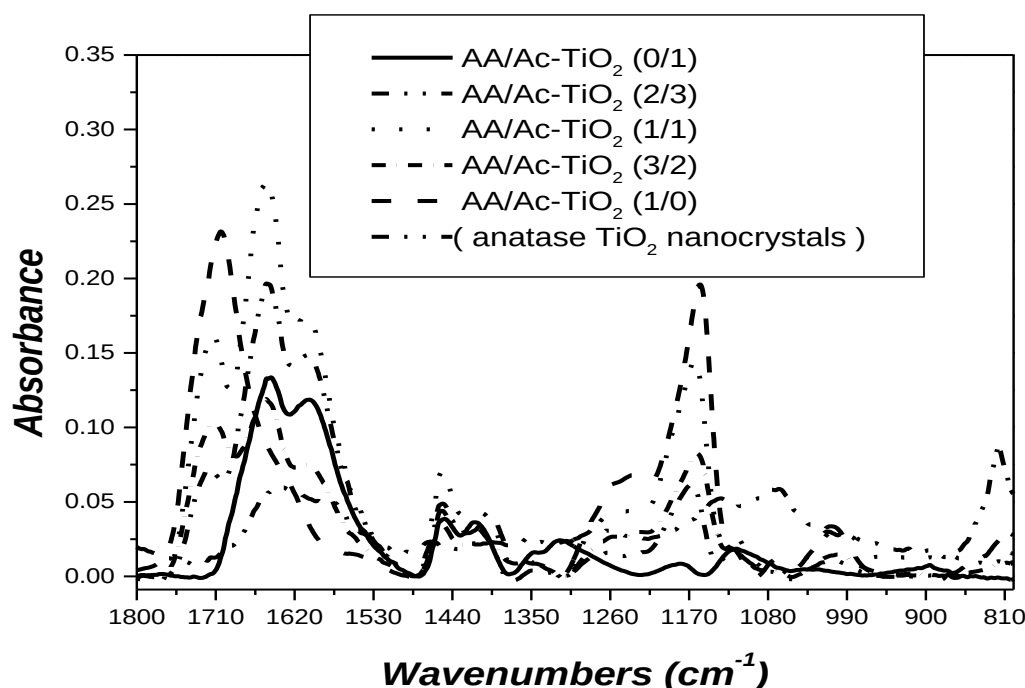
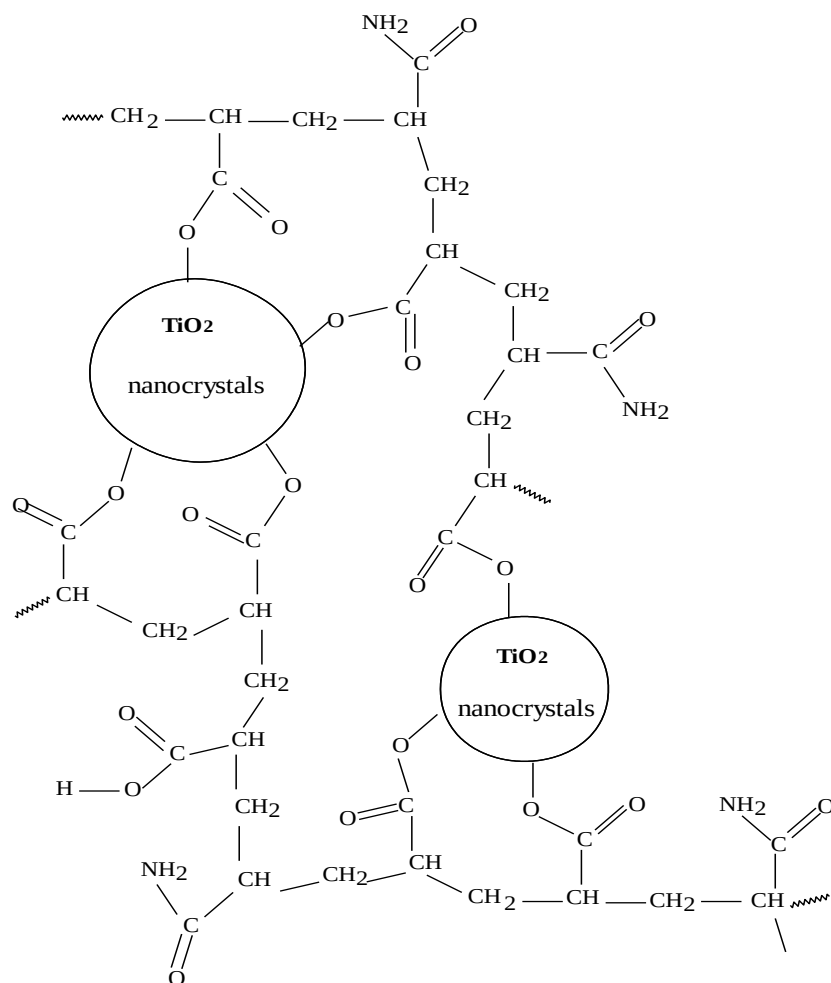


Figure 3. FTIR spectra of poly(AA-co-AAm)-TiO₂ hydrogels in different ratios

3.3. FTIR study of hydrogel

Figure 4 presents the FTIR spectra of P(AA-co-AAm)-TiO₂ (3%) hydrogels in different ratios (0/1, 2/3, 1/1, 3/2 and 1/0) from 1800 to 800 cm⁻¹. The most interesting bond from IR spectra of TiO₂-hydrogels nanocomposites are the absorption peak at 1004 and 1070 cm⁻¹ which may correspond to Ti-OH stretching motions and Ti-O-C bending, respectively [8]. The Ti-O-C may result from the interaction between the Ti-O-C network and the aliphatic chain of AA groups. Therefore stable bonding exists between the organic and the inorganic components.

The Figure 3, also shows that the characteristic absorption peak of anatase (1630 cm⁻¹), shifts to higher wavenumber (about 1652 cm⁻¹) after copolymerization. These results reveal that the nanocomposites are not the simple mixtures of polymer and TiO₂ nanocrystals. These should be strong interactions between the AA groups and nanoparticles, may be new chemical bonds are formed on the interface between poly(AA-co-AAm)-TiO₂ hydrogel and TiO₂ nanocrystals. See Scheme 1.



Scheme 1. Schematic structure of the ester like linkage between the hydrogel Poly(AA-co-AAm) and TiO_2 nanocrystals as predicted by IRTF spectroscopy.

3.4. Swelling behavior

Swelling capacity and kinetics of swelling of these hydrogels were studied and their corresponding swelling behavior was followed at pH 4, 7 and 8 in buffered solution at 310 K.

Results of these experiments indicated that the increase in weight of the swollen hydrogels is directly related to the duration of swelling. The swelling behavior observed could be associated with the absorption mechanism, which, in turn, is determined by the diffusion process. It is evident that the swelling ratio increases sharply upon prolongation of swelling time up to 100 minutes then levels off (not shown). Katime et al. ^[7], found that the swellability of the poly(AA-co-AAm) hydrogel increases at higher.

3.5. Kinetic study of swelling

The swelling kinetics of the prepared hydrogel was undertaken with view of clarifying the controlling mechanism of the swelling process. This was visualized through kinetic models.

The swelling mechanism of the samples was determined by applying the following equation:

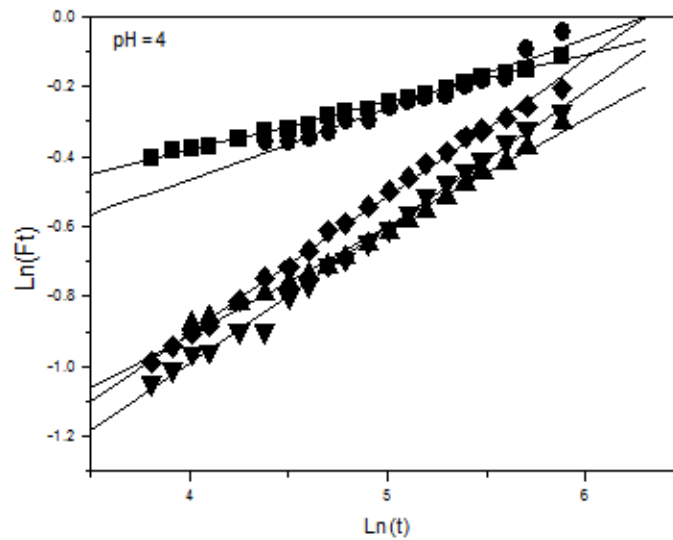
$$F_t = W_t / W_{\infty} = K t^n \quad (2)$$

Where K is the swelling constant and n is the swelling exponent calculated from the slopes of the lines of $\ln(F_t) = f(\ln(t))$ plots^[9]. Figure 5 illustrates the effect of AA/AAm ratio in presence of TiO_2 nanoparticles on the swelling characteristics of the prepared hydrogel.

A value of $n=0.5$ indicates a Fickian diffusion mechanism, while a value of $0 \leq n \leq 0.45$ or $0.45 \leq n \leq 1$ indicates that diffusion is anomalous. The values of swelling exponent n, obtained for the hydrogels AA/AC- TiO_2 , at different pH solutions, showed that the behavior of the hydrogels changes from the acidic to the alkaline solutions. Table 1.

Table1: Swelling data for poly(acrylic acid-co-acrylamide)- TiO_2 (3%) hydrogels at different ratios and pH.

Hydrogel ratios	pH=4	pH=7	pH=8	pH=4	pH=7	pH=8
	n			K (mn ⁻ⁿ)		
1/0	0.14	0.97	0.32	0.3964	0.00496	0.0453
3/2	0.20	0.72	0.20	0.2835	0.01900	0.0538
1/1	0.31	0.56	0.23	0.1181	0.03600	0.0712
2/3	0.39	0.45	0.24	0.0789	0.07316	0.0660
0/1	0.39	0.38	0.24	0.0852	0.14399	0.1258



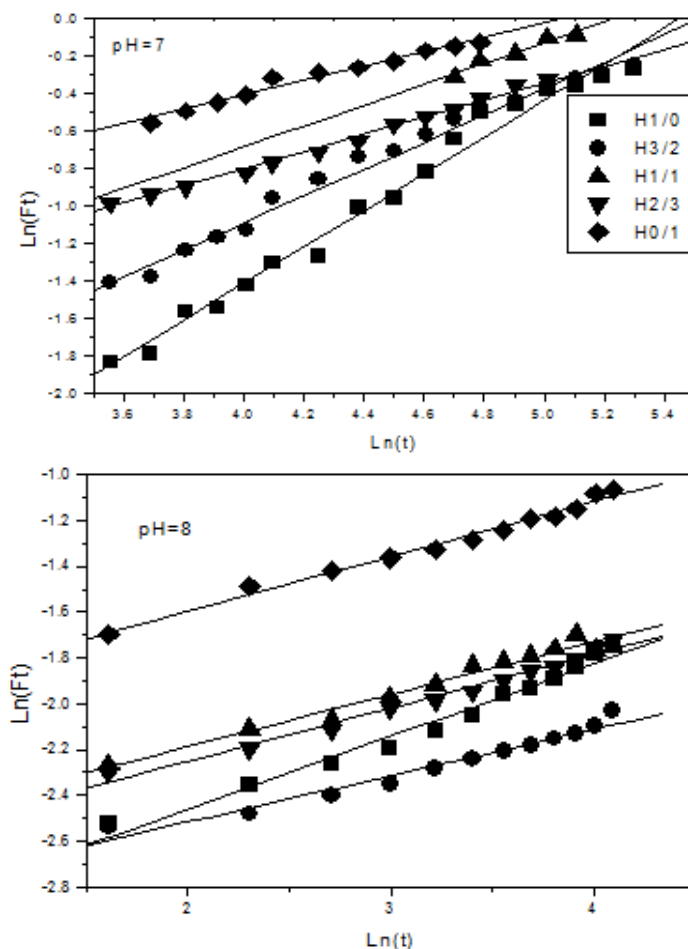


Figure 4. Swelling behavior of Poly(AA-co-AAm)-TiO₂ (3%) hydrogels at different ratios and different pH.

Results showed that the kinetic behavior of the studied hydrogel, doped with ceramic fillers, depends on the pH of the media. Figure 5a, shows that the diffusional exponent, n decrease when the concentration of (AAm) increase in the hydrogels synthesized at pH 4 and 7. Since the inverse phenomenon occurs at pH = 8. In the other hand the inverse event is observed for the variation of the kinetic constant K , as it can be observed in Figure 5b.

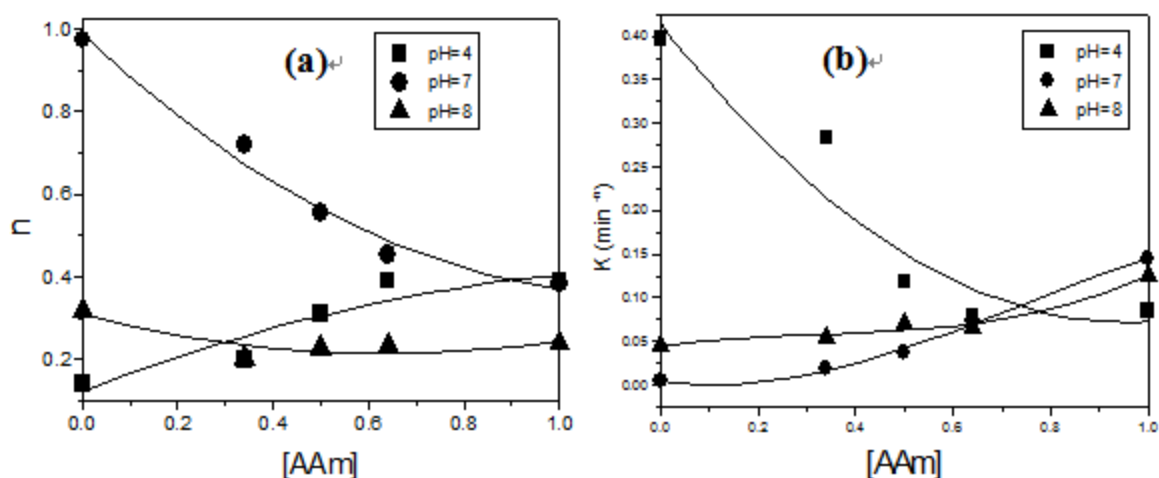


Figure 5. Variation of (a) the diffusional exponent n and (b) kinetic constants K , of Poly(AA/AAm)-TiO₂ (3%) hydrogels at different AAm composition and different pH.

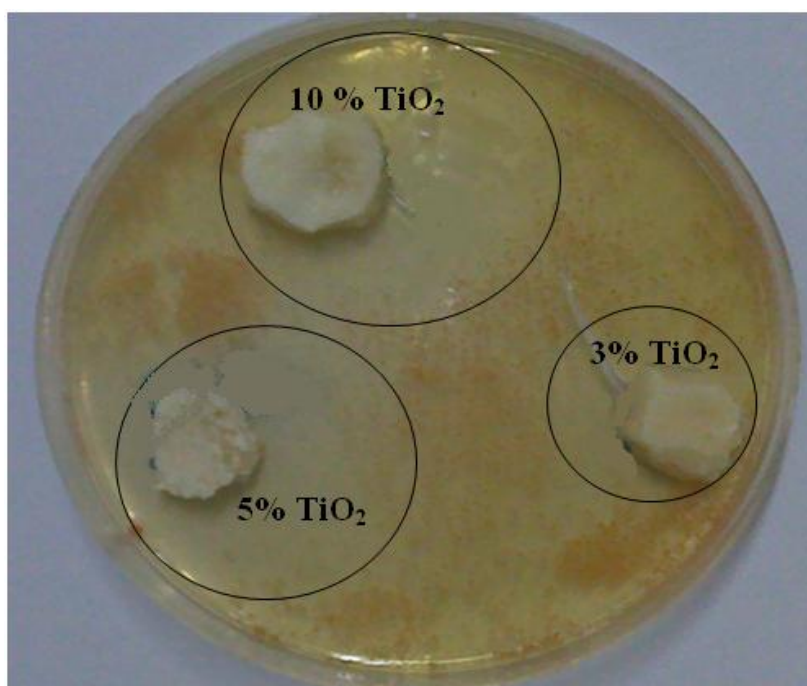


Figure 6. Photographs showing bacterial colonies in Petri plates containing AA-AAm(1/1)-TiO₂ hydrogels and the inhibiting zones created after 48h of incubation at different ratios of ceramic fillers.

3.6. Antibacterial propriety of TiO₂-hydrogel nanocomposites

A definite amount of nanocomposites obtained was tested against bacterial and fungal micro-organisms. The results as depicted in Figure 6, indicates that, when the concentration of TiO₂ increases in hydrogels the antibacterial activity of resulting nanocomposites also increase. It is clear that the

diameter of the inhibited zone around the hydrogels formed after incubation for 48 h increase with the increasing of the amount of TiO_2 in the hydrogels from 3 to 5%. Thus this diameter doesn't increase substantively when the amount of TiO_2 increases from 5 to 10%. This result indicates that optimal concentration of TiO_2 in the synthesized hydrogels might be 5%. Subsequently the TiO_2 -hydrogels nanocomposites can be used for antimicrobial applications in pharmaceutical field.

4. Conclusion

The composites prepared present a considerable consistency, even in hydrated media, since their swelling behavior is rather sensitive to the pH of the media. Specific polar interactions of the carboxylic groups of the hydrophilic acrylic acid component with the surface of TiO_2 particles modulate the behavior of the composites against the hydration processes at different pH. Size and distribution of the nanoparticles and their dependence on acrylamide/acrylic acid ratios as well as on the dose of TiO_2 were considered using Scanning Electron Microscopy (SEM). The X-ray diffraction patterns showed the presence of TiO_2 nanoparticles with tetragonal body centered structure. Furthermore, the antimicrobial and antifungal activities of the hydrogels were reported. These results suggest that TiO_2 -Hydrogel can be used as effective growth inhibitors in various micro-organisms, making them appropriate to diverse medical devices and antimicrobial control systems.

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Treatment of wastewater from alkaline degreasing by heterogeneous photocatalysis with water reuse

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Abstract. The nonylphenol ethoxylate (NP_nEO) surfactant is used in the alkaline degreasing in the electroplating industry. It is considered an emerging organic pollutant (EOP), endocrine disrupter and recalcitrant. Aiming the degradation of this pollutant, in order to reuse the water from alkaline degreasing, in this work, the use of photo-catalyst TiO₂/Ti of De Nora of Brazil® was evaluated in heterogeneous photocatalytic processes under irradiation of mercury vapor lamps of high pressure with different powers (125 W and 250 W). The degradation of this surfactant was monitored by UV/Visible spectroscopy and the mineralization by Total Organic Carbon (TOC). The energetic consumption and the reaction kinetics were calculated. The results of UV/Visible spectroscopy shows a characteristic band relative of the surfactant in the initial wastewater and, at the final time of the treatment, it is not possible the identification of this band. In the TOC, at the final treatment time (240 minutes) one notes a mineralization of this surfactant of about 33% and 63%, when 125 W and 250 W lamps were respectively used. The energetic consumption of the 125 W lamp is higher than the 250 W lamp (8.17 kW h m⁻³ order⁻¹ and 1.65 kW h m⁻³ order⁻¹) due to their lower efficiency in photo-excitation of the catalyst. Besides, the reaction kinetics for the 125 W and 250 W lamps is 0.10 min⁻¹ and 0.25 min⁻¹. With this, we can infer that the use of heterogeneous photocatalysis using the TiO₂/Ti catalyst under irradiation of 250 W lamp is an alternative to the destruction of this surfactant, thus being possible the reuse of water as process water.

Keywords: Emerging organic pollutant; Heterogeneous Photocatalysis; Water reuse

1. Introduction

The increasing demand for water has made the water reuse a current topic of great importance. In this context, wastewater and treated effluents have a fundamental role in planning and sustainable

management of water resources as a substitute for the use of water for some industrial purposes¹. To the reuse of water, it is necessary to develop new technologies.

Studies indicate the use of the photocatalysts in the heterogeneous photocatalysis (HP) process as a promising technology to this treatment. The HP process consists of the catalysis of photochemical reactions on the surface of a semiconductor, involving two simultaneous reactions, oxidation by gaps in the valence band (VB) and reduction by photo-generated electrons in the conduction band (CB) of the semiconductor². The photocatalytic activity starts with the process of charge separation that occurs under UV irradiation.



The interaction of this pair with donor/receptor substances for electron promotes oxidation and reduction reactions at the semiconductor surface. In general, the electrons react with oxygen, while the gaps generate HO· in water³.



With that, the electrons generated in CB can react with oxygen, producing a superoxide ($\text{O}_2 \cdot^-$) (reaction 5) and the sequence of reactions promotes the formation of hydrogen peroxide (H_2O_2)⁴. The generation of oxidants, for example hydroxyl radical ($\text{HO} \cdot$), is associated to the degradation of a large number of emerging organic pollutants (EOP).

The EOP are chemical compounds present in a variety of commercial products such as surfactants. These pollutants are not usually monitored or are not regulated by legislation, but they present risks to human health and to the environment. Among these EOP, we can highlight the nonylphenol ethoxylate (NP_nEO), a nonionic surfactant used in the alkaline degreasing of the electroplating industry. This surfactant has a recalcitrance and a toxicity that increases with decreasing number of ethoxylate groups, process that occurs when it is biodegraded. Some of the products of biodegradation are the nonylphenol with 4, 3, 2 or 1 degree of ethoxylation and nonylphenol (NP), which are considered endocrine disruptor mimicking the natural hormone 17 β -estradiol.

The aim of this study was to evaluate the use of the commercial photocatalyst TiO_2/Ti of De Nora of Brazil® in Heterogeneous Photocatalysis process, as well as optimize its operating parameters in order to plan the direct reuse of the wastewater from the electroplating alkaline degreasing industry containing the nonylphenol ethoxylate (NP_nEO) surfactant.

2. Experimental methods

2.1. Initial effluent

In order to simulate the wastewater from the alkali degrease of the electroplating industry, a wastewater containing NP₄EO commercial surfactant was prepared by dilution of the commercial product Ultralex NP40® up to a concentration of 51 mg L⁻¹.

2.2. Heterogeneous photocatalysis system

The photocatalytic reactor used in this process is borosilicate glass, jacketed, connected to a thermostat for temperature control and operated in a batch mode. As photocatalyst, it was used a commercial mesh composed by TiO₂/Ti of De Nora of Brazil®. The UV radiation sources are high-pressure mercury vapor lamps, without the outer glass bulb, of 125 W and 250 W, coupled to a quartz bulb. The lamp, quartz bulb and TiO₂/Ti mesh group is placed concentrically in the reactor, remaining under negative irradiation (figure 1).

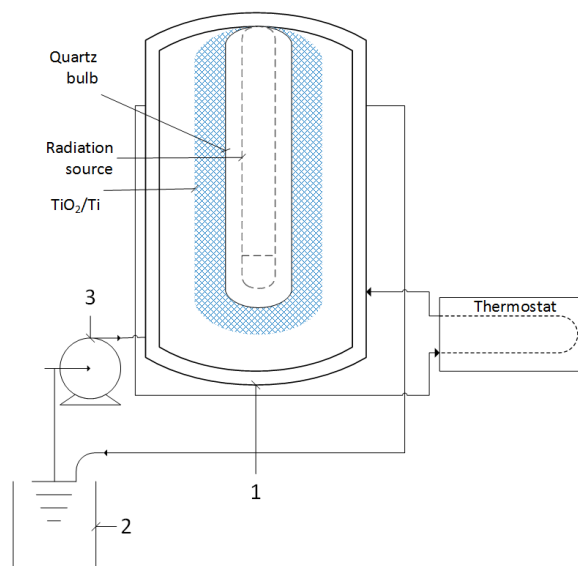


Fig 1. Batch photo-reactor used in the HP process, where 1 is a jacket borosilicate glass reactor, 2 is a reservoir and 3 is a peristaltic pump.

For all processes, 5 L of the initial wastewater was placed into a reservoir that feeds the reactor via a peristaltic pump at a flow rate of 1 L min⁻¹. All procedures were repeated five times and their settings are shown in table 1.

Table 1 Configuration of the heterogeneous photocatalytic processes.

Configuration	Lamp power (W)	Catalyst	Treatment time (minunes)
HP1	250	TiO ₂ /Ti De Nora of Brazil®	0, 60, 120, 180 and 240
HP2	125	TiO ₂ /Ti De Nora of Brazil®	0, 60, 120, 180 and 240

2.3. Analysis

The initial wastewater and the one treated by the HP processes were characterized by different analytical methods: UV/Visible spectroscopy (*T80+ UV/Vis Spectrometer from PG Instruments Ltd*), pH (*potentiometric method - DM-22 Digimed*) and Total Organic Carbon (TOC) (*TOC-L CPH Shimadzu*). In order to identify the degradation products, gas chromatography – flame ionization detector (GC/FID) was performed using a GC 17A (*Shimadzu*) apparatus under the following conditions: column RXI 5ms - 30m x 0.25mm x 0.25µm. The extractions were performed as described by M. Ahel, T. ConradW. Giger ⁵.

The efficiencies of degradation (Ed) were calculated in relation to the absorbance values presented in the results of UV/Visible spectroscopy according to the equation⁶:

$$Ed = \frac{Abs_i - Abs_f}{Abs_i \times 100} \quad (1)$$

where Ed is the degradation efficiency; Abs_i is the initial absorption and Abs_f is the final absorption.

The reaction kinetics were calculated based on the TOC results and calculated by the *Langmuir-Hinshelwood* equation⁷⁻¹⁰:

$$\ln \frac{C}{C_0} = K' \cdot t \quad (2)$$

where t is the exposure time; K' is the constant of the first order; C_0 is the TOC of the initial wastewater and C is the TOC of the final wastewater.

According to J. R. Bolton, K. G. Bircher, W. TumasC. A. Tolman ¹¹, one can also calculate the electric energy per order (E_{EO}), defined as the electric energy in kilowatt hours (k W h) required to degrade a contaminant by one order of magnitude in a unit volume of 1 m³ of contaminated water, as described by:

$$E_{EO} = \frac{P \cdot t_f \cdot 1000}{V \cdot 60 \cdot \ln \left(\frac{C_0}{C} \right)} \quad (3)$$

where P is the power (k W); V is the treated volume (L) and t_f is the process time (min);

The absolute measurement of incident irradiance (E) in W m⁻² of ultrapure water and of the initial wastewater were determined to the high-pressure commercial mercury vapor lamps (125 W and 250 W) by an *Instrutherm MRUR-203 UV light meter*.

Incident irradiance (W m⁻²) can be converted to quantum flux (also called photon flux) using the Plack's equation:

$$E_p = \frac{h \cdot c}{\lambda} \quad (4)$$

where, h is the Planck's constant (6.626×10^{-34} J s), c is the speed of light (2.998×10^8 m s⁻¹) and λ is the wavelength (m) based on the photometric data of the 125 W and 250 W lamps used in this work, $\lambda = 365$ nm).

Using these values, $E_p = 5.44 \times 10^{-19}$ J. The number of photons (N_p) can be then calculated by:

$$N_p = \frac{E}{E_p} \text{ (m}^{-2}\text{s}^{-1}\text{)} \quad (5)$$

Having the N_p value, the photon flux (E_{qf}) will be determined by:

$$E_{qf} = \frac{N_p}{N_A} (\mu\text{mol m}^{-2} \text{s}^{-1}) \quad (6)$$

where N_A is the Avogadro number ($N_A = 6.02 \times 10^{23} \text{mol}^{-1}$).

3. Results and discussion

3.1. Initial and treated wastewater characterization

The spectrum of the initial wastewater and the wastewater treated at the final time of the treatment (240 minutes) by the heterogeneous photocatalysis processes are shown in figure 2.

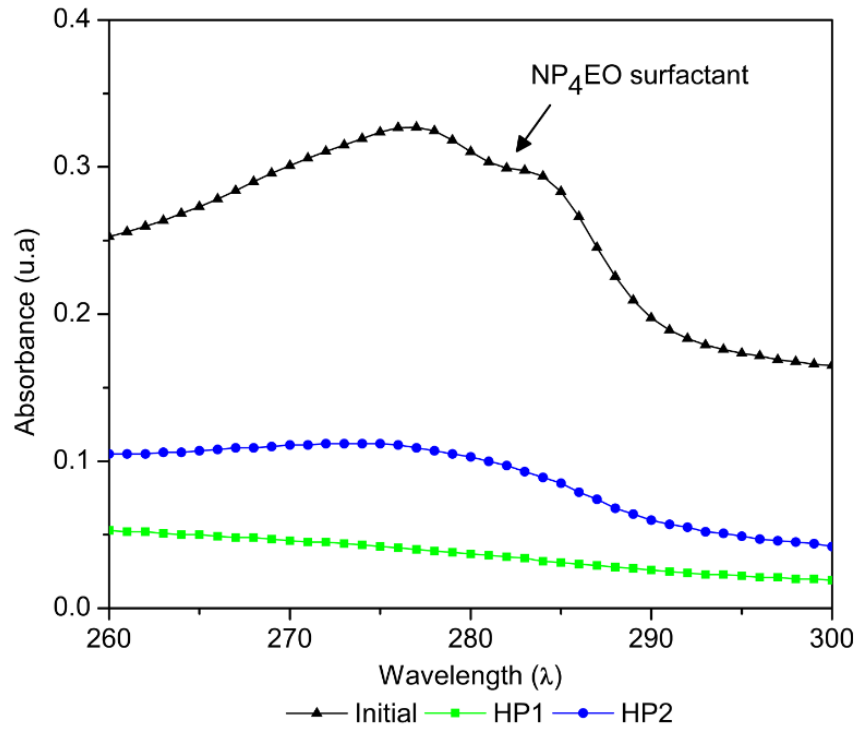


Fig. 2. UV/Visible spectroscopy analysis of the initial wastewater and of the wastewater treated by HP processes at the final time (240 min).

For the initial wastewater, in figure 2 it is noted a band in wavelengths between 270 nm – 290 nm relating to a NP₄EO surfactant band. This band was also defined on work carried out by J. Kim, G. V. KorshinA. B. Velichenko¹². At the final time of the treatment (240 minutes), for both configurations, it is noted that the band related to the surfactant can no longer be identified, thus demonstrating the degradation of the surfactant for both HP1 and HP2 configurations.

In relation to figure 2 and on the basis of equation 1, it can still be observed that the HP1 process, which used the 250 W lamp, obtained a higher degradation of the surfactant (87%), when compared to HP2 process, which used the 125 W lamp (66%).

In fact, the UV/Visible spectroscopic and the TOC analysis are complementary between themselves, once in the UV/Visible analysis it is possible to monitor the degradation of the surfactant, whereas the TOC analysis aim to monitor the surfactant mineralization in carbon dioxide (CO₂), water (H₂O) and inorganic ions¹³.

In figure 3, one can visualize that the HP1 process that has used the 250 W lamp obtained a reduction of 63% on TOC, while the HP2 process that has used the 125 W lamp obtained a TOC reduction of 33%. It is noted that there is not a complete mineralization of the surfactant because the NP₄EO degradation can generate reaction intermediates such as organic acids, ethylene glycol, polyethylene glycol, alcohols, NP and others¹⁴⁻¹⁶_ENREF_8. The HP process can be used, even if not completely mineralizing the surfactant, provided that the degradation products are biodegradable and less toxic than their precursors.

The TOC results (figure 3) resemble those of UV/Visible results (figure 2), i.e. the HP1 configuration (250 W) showed better results in degradation and mineralization of the surfactant.

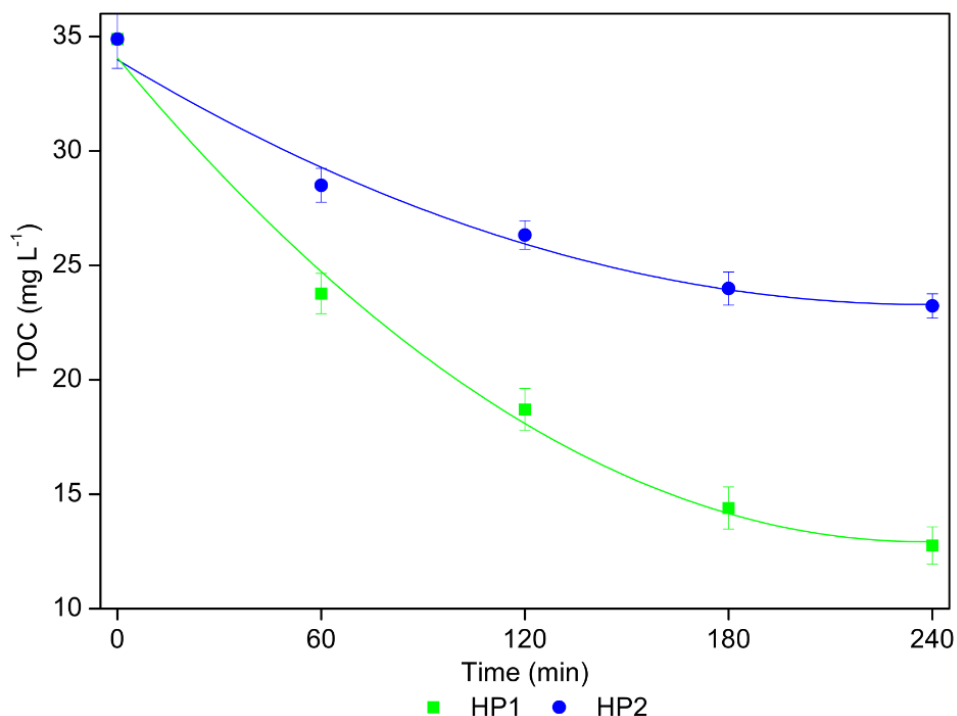


Fig 3. TOC of the initial wastewater and wastewater treated by HP processes.

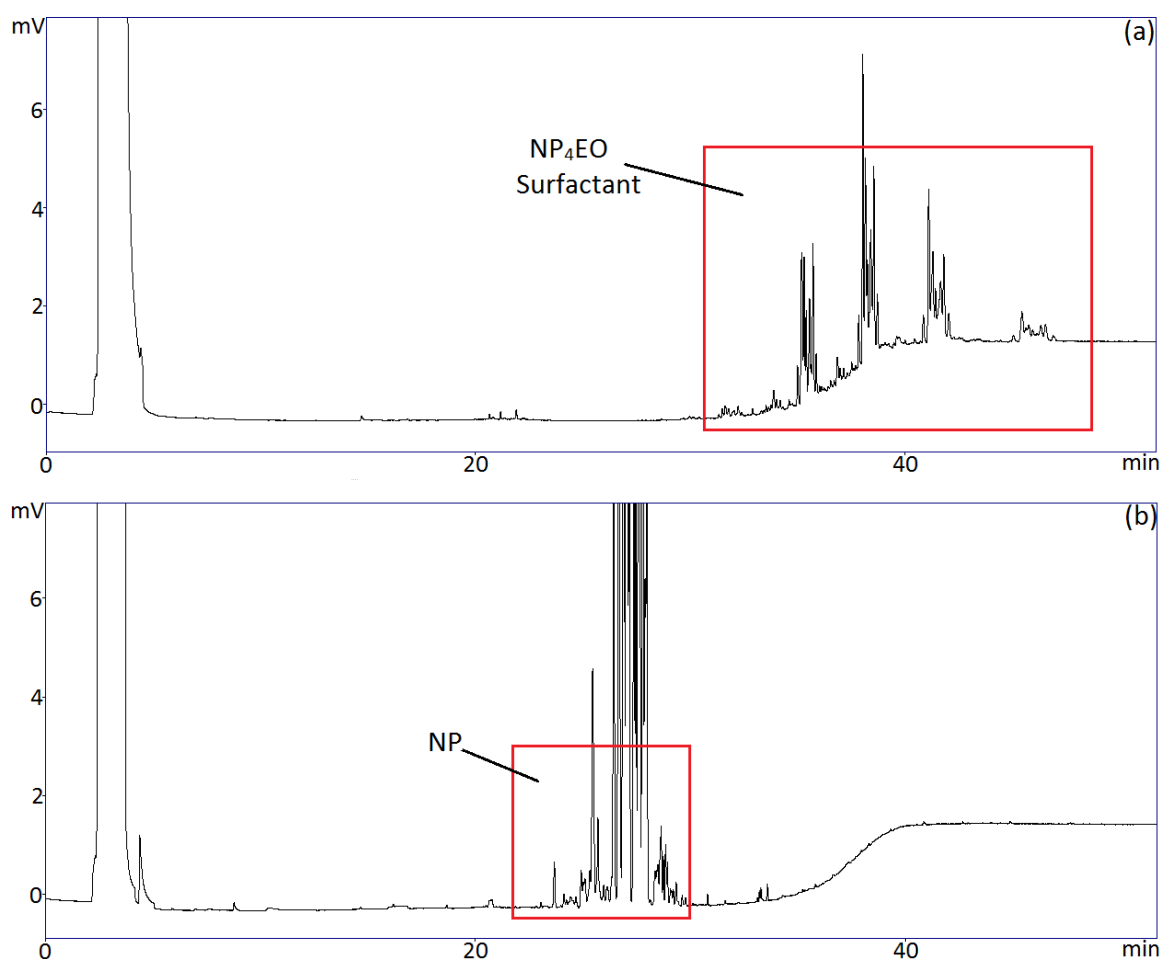


Fig 4. Chromatograms of the NP₄EO surfactant standard (a) and NP standard (b).

In order to verify the degradation of the NP₄EO surfactant and their degradation products, gas chromatography couple to flame ionization detector (GC-FID) was performed. The evaluation was performed by means of identification of the peaks in the sample, based on the chromatographic patterns of the NP₄EO surfactant (Ultranex NP40®) contained in the initial wastewater (figure 4 (a)), and the NP (Sigma-Aldrich) (figure 4 (b)). For better visualization of the peaks, all chromatograms were magnified.

In figure 4 (a) one can visualized peaks characteristics of the NP₄EO surfactant in the retention times from 31 minutes to 47.5 minutes, whereas in figure 4 (b) it can be visualized characteristic peaks of NP in the retention time from 23 minutes to 30 minutes.

Figure 5 (a) and 5 (b) shows chromatograms of the wastewater treated by the HP1 (250 W) and HP2 (125 W) process, respectively, at the final treatment time (240 minutes).

In figure 5 (a) and (b) one can be observed the degradation of the NP₄EO surfactant, when compared to the initial wastewater (figure 4 (a)). Besides, in figure 5 (a) it can be noted a higher degradation of the NP₄EO surfactant, when compared to figure 5 (b), i.e. there is a higher degradation of the surfactant when using the HP1 process. It should be noted also a possible formation of more toxic metabolite NP, therefore, it becomes necessary a more refined data analysis.

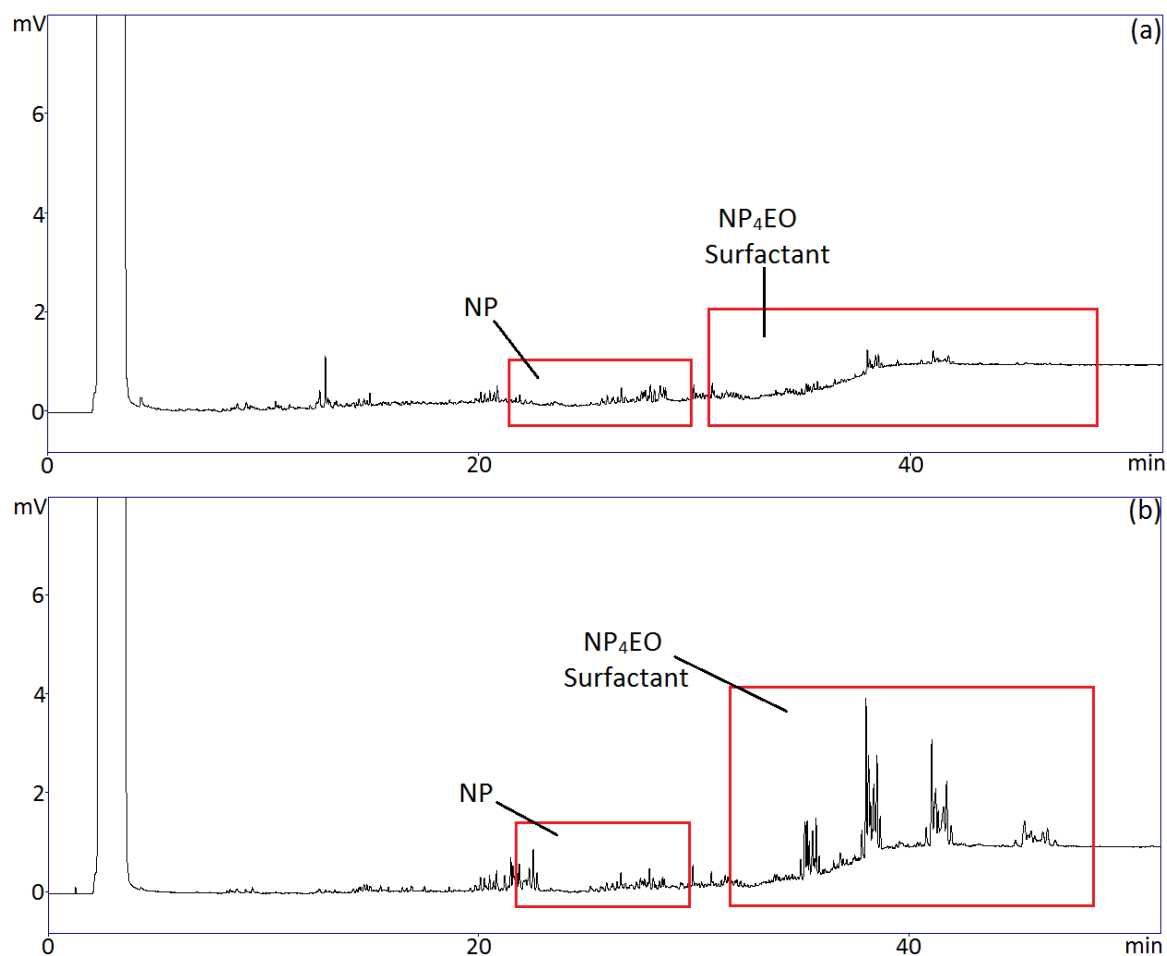


Fig 5. Chromatograms of the wastewater treated at the final time (240 min), **(a)** by HP1 process and **(b)** by HP2 process.

3.2. Kinetic reaction and energy consumption

The reaction kinetics is an important point to be studied because it includes investigations of how different experimental conditions can influence of the rate of the chemical reactions. The kinetic can receive the influence the following parameters: concentration of the reactants, presence or not of the reagent solution, temperature, electricity, light, pressure, the presence of catalysts, as well the presence of reaction products.

Figure 6 shows the effect of different UV radiation sources (250 W and / or 125 W) in the reaction kinetics.

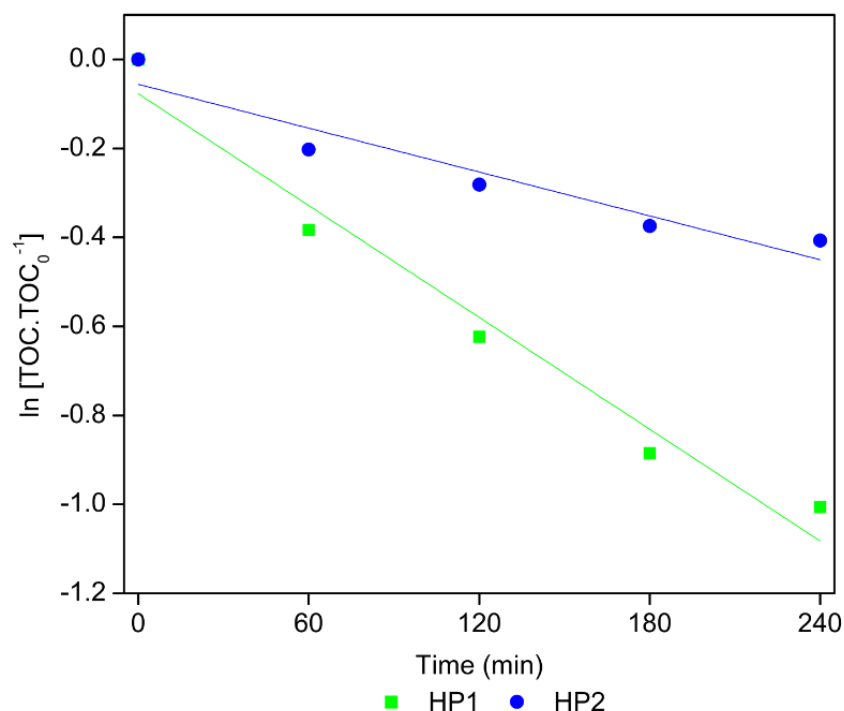


Fig 6. Reaction kinetics to the degradation of NP₄EO surfactant by HP processes.

It is observed in figure 6, that there is a high increase in the reaction kinetics when increasing the lamp power (UV radiation source) of 125 W to 250 W, and the K' value for the HP1 and HP2 processes were 0.25 min^{-1} and 0.10 min^{-1} , respectively. This study is justified because the reaction kinetics is related to the rate with which the NP₄EO surfactant is degraded, thus affecting the residence time of the wastewater in the photo-reactor. Thus, HP1 process requires a smaller residence time in the photo-reactor to degrade the same amount of NP₄EO surfactant than the HP2 process.

The use of different source lamps in the processes of HP turns necessary the calculation of the energy consumption to treat 1 m^3 of contaminated wastewater, as this is an important parameter for the overall cost of the process. The energy consumption was calculated according to equation 3 and the results for the HP1 and HP2 processes were: $1.65 \text{ kW h m}^{-3} \text{ order}^{-1}$ and $8.17 \text{ kW h m}^{-3} \text{ order}^{-1}$.

It is noted here that although the nominal power of the radiation source of HP1 process is much higher than that used in the HP2 process, the HP1 process exhibits a less energy consumption, when compared to HP2 process. This can be explained because the HP1 process (250 W) obtained the best results in UV/Visible spectroscopy, TOC, GS-FID and K' .

3.3. Influence of the UV radiation source

In order to evaluate the influence of the UV radiation sources, the incident irradiance was measured and the number of photons (N_p) and the photon flux (E_{qf}) were calculated for both solutions (ultrapure water and initial wastewater) and the results are shown in table 2.

Table 2 Influence of the UV radiation source in different environments.

Catalyst	Lamp power	Environment	E	E_p	N_p	E_{qf}
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	(W)		(W m ⁻²)	(J)	(m ⁻² s ⁻¹)	(mol m ⁻² s ⁻¹)
TiO₂/Ti De Nora of Brazil®	250	Ultrapure water	5.85	5.44 x 10 ⁻¹⁹	1.07 x 10 ⁺¹⁹	1.78 x 10 ⁻⁵
		Initial wastewater	4.65	5.44 x 10 ⁻¹⁹	8.54 x 10 ⁺¹⁸	1.41 x 10 ⁻⁵
	125	Ultrapure water	1.03	5.44 x 10 ⁻¹⁹	1.89 x 10 ⁺¹⁸	3.14 x 10 ⁻⁶
		Initial wastewater	0.95	5.44 x 10 ⁻¹⁹	1.74 x 10 ⁺¹⁸	2.89 x 10 ⁻⁶

For the 250 W and 125 W lamps, the photon flux that arrives to the catalyst surface through the ultrapure water is 1.78 x 10⁻⁵ mol m⁻² s⁻¹ and 3.14 x 10⁻⁶ mol m⁻² s⁻¹, respectively. For the same lamps, the photon flux that arrives to the catalyst through the initial wastewater is 1.41 x 10⁻⁵ mol m⁻² s⁻¹ and 2.89 x 10⁻⁶ mol m⁻² s⁻¹. Then, it is possible to see that the initial wastewater absorbs some radiation, favoring consequently the heterogeneous photocatalysis.

One notes that the HP1 process (250W) obtained the best results, and analyzing the results of table 2, one can attribute this fact to the photon flux that reaches the surface of the catalyst, which is much higher when using lamp 250 W.

4. Conclusions

Analyzing the results it was concluded that the HP1 process, using 250 W lamp, showed best results in degradation and mineralization of the NP₄EO surfactant, when compared to the HP2 process (125 W). The HP1 process presented also the highest reaction kinetics by a smaller the residence time of the wastewater in the photo-reactor as well as a lower presenting energy consumption. These results were related to the increased amount of photon flux generated, which are able to reach the surface of the catalyst, thereby increasing the efficiency of the process.

Considering that the 240 minutes treatment was not sufficient for complete degradation of the surfactant, it becomes necessary to increase the treatment time. With the increase in treatment time, the HP1 process emerge as an alternative for the treatment of wastewater from the alkaline degreasing of the electroplating industry, thus being possible the water reuse.

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Investigation on effect of pulsed current MPAW parameters on weld quality characteristics at various thicknesses of AISI 304L Sheets

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Abstract: Micro Plasma Arc Welding (MPAW) is one of the important arc welding process commonly using in sheet metal industry for manufacturing metal bellows, metal diaphragms etc. In the present paper welding of AISI 304L austenitic chromium-nickel stainless steel using pulsed current micro plasma arc welding was discussed. The paper mainly focuses on studying the effect of parent metal thickness on weld quality characteristics like weld pool geometry parameters, microstructure, grain size, hardness and tensile properties of Pulsed Current Micro Plasma Arc Welded AISI 304L austenitic stainless steel sheets. Results reveals that for a peak current of 7 Amperes, back current of 4 Amperes, pulse rate of 40 pulses /second and pulse width of 50%, 0.25 mm thick AISI 304L sheets has optimal weld quality characteristics.

Key Words: Pulsed current micro plasma arc welding, AISI 304L, grain size, hardness, tensile properties.

1. INTRODUCTION

Austenitic stainless steels are particularly prone to the hot cracking phenomenon. It has been determined however, that hot cracking may be reduced in austenitic stainless steel weldments by using filler materials that contain a small percentage of retained ferrite [1-3]. Although appropriate filler materials have been developed, problems still arise especially in the root of weldments, where the filler material may be diluted by the high amount of austenite in the parent material. Furthermore, the slower

cooling rate at the root with respect to the rest of the weld nugget reduces the amount of retained ferrite and increases the likelihood of hot cracking [2,3].

While filler materials are able to compensate for undesired changes in the microstructure of the solidified region and cannot prevent the microstructural changes in the HAZ. When steel is held at critical temperature range (600-800 °C) chromium precipitates out of the matrix and forms chrome carbides along the grain boundaries. The formation of chrome carbides produces a chemical inhomogeneity in the surrounding grains and become depleted in chromium with respect to the base material. When these precipitates cause the surrounding areas to have less than about 13 wt. % chromium, the areas become susceptible to corrosion. Low carbon content reduces this problem by reducing the amount of chromium being precipitated along the grain boundaries.

When post-weld annealing is possible, high carbon grades may be used. While a solid solution heat treatment may be used to force the precipitates back into solution, and restore the chemical homogeneity, which is not always possible. This is an acceptable method when the parts may be protected from oxidation and won't be affected by distortion and is impractical for large structures or field repairs. In these cases an "L" grade austenitic stainless steel is preferred.

P. Johan Singh et al. [4] evaluated fatigue life on GTAW load-carrying cruciform joints of AISI 304L stainless steel with Lack of Penetration (LOP) using conventional S-N and crack Initiation-Propagation (I-P) methods. Nattapong Sonsuvit et al. [5] investigated the effects of Tungsten Inert Gas (TIG) pulse welding parameters and nitrogen gas mixed in Argon shielding gas on weld bead formation and microstructure of weld metals of AISI 304L stainless steels at the 10-h welding position. The latter result implies the possibility to mix nitrogen gas in argon shielding gas in order to modify the ratio of δ -ferrite in austenite matrix. M. Ahmad et al. [6] reported that $Zr(Cr, Fe)_2$ intermetallic compound and Zr_2Fe-Zr_2Ni eutectic phases have been observed in the molten zone of the TIG welded joints of the Zircaloy-4 and stainless steel 304L. P.Johan Singh et al. [7] conducted fatigue tests for gas metal arc welded (GMAW) butt joints of AISI 304L stainless steel with reinforcement using fracture mechanics. Constant amplitude fatigue tests with stress ratio ($R=0$) were carried out. The predicted fatigue lives were compared with the experimental values. This study suggested that the crack growth parameters are dependent on the crack propagation directions for the same material. Woei-Shyan Lee et al. [8] studied the impact properties of 304L Stainless Steel SMAW joints at strain rates between $10^{-3} s^{-1}$ and $7.5 \times 10^3 s^{-1}$ using a compressive split-Hopkinson bar. Velasco, F et al. [9] analysed the effect of welding on mechanical properties of ribbed bars of two cold-deformed austenitic stainless steels (low-nickel AISI 204Cu and traditional 304L types) and two duplex stainless steels (SAF 2205 type, cold and hot-worked). Woei-Shyan Lee et al. [10] used split-Hopkinson pressure bar to investigate the effects of strain rate in the range of $10^{-3} s^{-1}$ to $8 \times 10^{-3} s^{-1}$ and welding current mode upon the dynamic impact behavior of PAW 304L stainless steel (SS) weldments.

From the earlier works reported on AISI 304L austenitic stainless steel, it is understood that selection of welding process parameters play a vital role in obtaining the desired weld quality. Hence, an attempt is made to study the welding quality characteristics. The present paper focuses on studying the weld quality characteristics like weld pool geometry parameters, microstructure, grain size, hardness and tensile properties of Pulsed Current Micro Plasma Arc Welded AISI 304L austenitic stainless steels.

2. EXPERIMENTAL PROCEDURE

Austenitic stainless steel (AISI 304L) sheets of thicknesses 0.15 mm, 0.2 mm, 0.25 mm, 0.3 mm are welded autogenously with square butt joint without edge preparation. The chemical composition of AISI 304L stainless steel sheets considering all the thickness is given in Table 1. High purity argon gas (99.99%) is used as a shielding gas and a trailing gas right after welding to prevent absorption of oxygen and nitrogen from the atmosphere. The welding has been carried out under the welding conditions presented in Table 2. There are many influential process parameters which effect the weld quality characteristics of Pulsed Current MPAW process like peak current, back current, pulse rate, pulse width, flow rate of shielding gas, flow rate of purging gas, flow rate of plasma gas, welding speed etc. From the earlier works of Kondapalli Siva Prasad et al. [11-14] carried out on Pulsed Current MPAW it was understood that the peak current, back current, pulse rate and pulse width are the dominating parameters which effect the weld quality characteristics. The values of process parameters used in this study are the optimal values obtained from our earlier papers [11-14]. Hence peak current, back current, pulse rate and pulse width are chosen and their values are presented in Table.3.

Table 1 Chemical composition of AISI 304L (weight %)

C	Si	Mn	P	S	Cr	Ni	N	Fe
0.021	0.35	1.27	0.030	0.001	18.10	8.02	0.053	72.155

Table 2 Welding conditions

Power source	Secheron Micro Plasma Arc Machine (Model: PLASMAFIX 50E)
Polarity	DCEN
Mode of operation	Pulse mode
Electrode	2% thoriated tungsten electrode
Electrode Diameter	1mm
Plasma gas	Argon & Hydrogen
Plasma gas flow rate	6 Lpm
Shielding gas	Argon
Shielding gas flow rate	0.4 Lpm
Purging gas	Argon
Purging gas flow rate	0.4 Lpm
Copper Nozzle diameter	1mm
Nozzle to plate distance	1mm
Welding speed	260 mm/min
Torch Position	Vertical
Operation type	Automatic

Table 3 Important weld parameters

Serial No	Input Factors	Unit	Value
1	Peak Current	Amperes	7
2	Back Current	Amperes	4
3	Pulse rate	Pulses/second	40
4	Pulse width	%	50

2.1. Measurement of Weld Bead Geometry

Three metallurgical samples are cut from each joint leaving the edges of defective portion of the welded length. Defective length of weld is identified visually and also by conducting dye penetrant and X-ray tests and mounted using Bakelite. Sample preparation and mounting is done as per ASTM E 3-1 standard. The transverse face of the samples are surface ground using 120 grit size belt with the help of belt grinder and polished sequentially using grade 1/0 (245 mesh size), grade 2/0 (425 mesh size) and grade 3/0 (515 mesh size) sand paper. The specimens are further polished using aluminum oxide, diamond paste and velvet cloth on a disc polishing machine. The polished specimens are macro-etched using 10% Oxalic acid solution to reveal the geometry of the weld bead (Figure 1). Several critical parameters, such as front width, back width, front height and back height of the weld bead geometry are measured using Metallurgical Microscope (Make: Dewinter Technologie, Model No. DMI-CROWN-II) at 100X magnification. The measured bead geometry dimensions are presented in Table.4

Figure's 2a, 2b, 2c indicate the welded joints for thickness of 0.15 mm, 0.2 mm, 0.25 mm and 0.3 mm respectively.

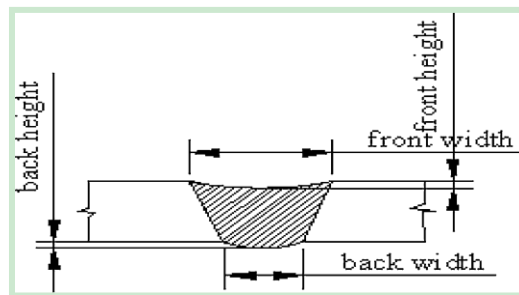


Fig.1 Typical weld bead geometry

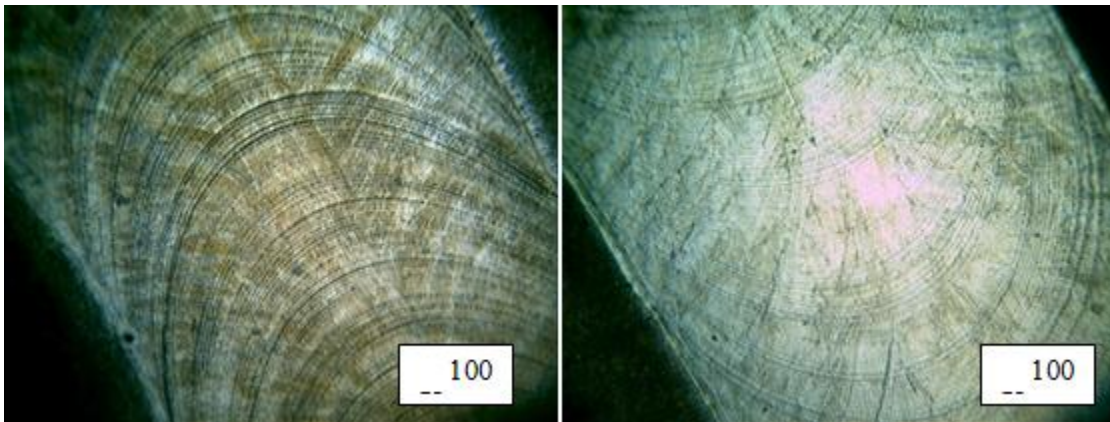


Fig.2a weld bead at 0.15 mm thick

Fig.2b weld bead at 0.2 mm thick

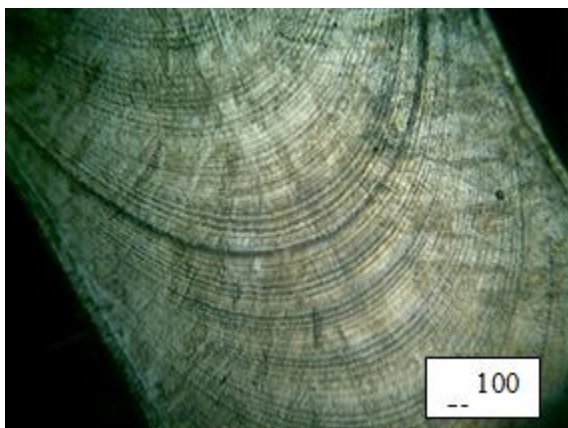


Fig.2c weld bead at 0.25 mm thick

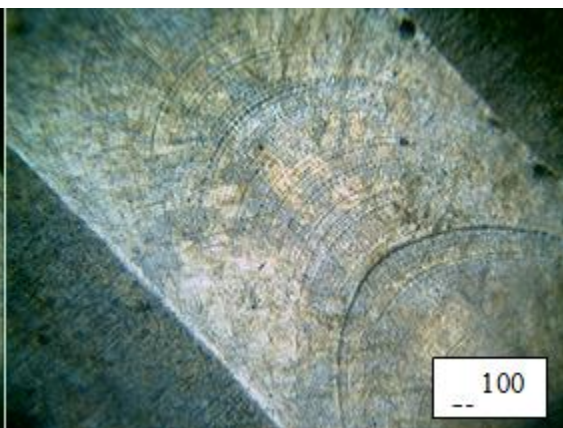


Fig.2d weld bead at 0.3 mm thick

The samples were cut in transverse direction from the welded specimens to study the depth of penetration and fusion and are presented in Figure.2e to 2h.

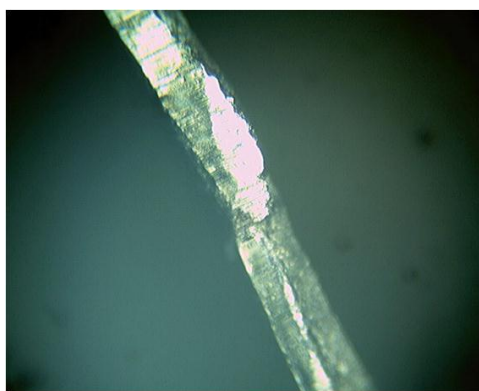


Fig.2e 0.15 mm thick weld



Fig.2f 0.2 mm thick weld

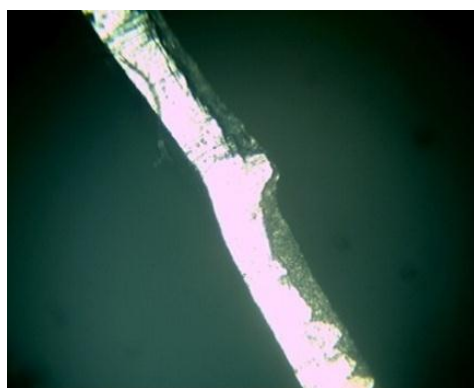


Fig.2g 0.25 mm thick weld

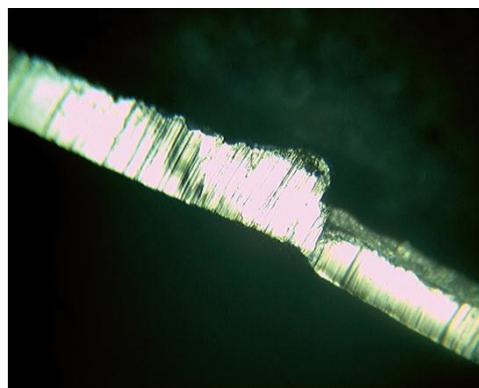


Fig.2h 0.3 mm thick weld

Table 4 Comparison of weld bead geometries

Parent metal thickness (mm)	Weld pool Geometry			
	Front Width (mm)	Back Width (mm)	Front Height (mm)	Back Height (mm)
0.15	1.547	1.474	0.042	0.038
0.20	1.561	1.537	0.048	0.030
0.25	1.509	1.439	0.060	0.047
0.30	1.061	0.922	0.038	0.031

From Fig.2a , 2b , 2c & 2d it is understood that the weld bead is more for 0.15 mm thick AISI 304L sheet and keeps on increasing up to 0.25 mm thick for the same heat input. However for thickness of 0.3mm it is observed that there is improper fusion, because of higher thickness of the base metal. The peak current of 7 Amperes is not sufficient to fusion weld 0.3 mm thick AISI 304L sheets.

2.2. Microstructure and Grain Size measurement

In order to reveal the microstructure and grains, polishing was done according to standard Metallurgical procedure and Etching was done as per ASTM E407. Electrolytic etching was done using 10% Oxalic acid for about 1 minute. Microstructures are captured using Metallurgical Microscope and presented in Figure.3. Scanning Electron Microscope (SEM), Make: INCA Penta FETx3, Model: 7573 is used to measure the fusion zone grain size and parent metal. Figure 4a, 4b, 4c & 4d indicates the fusion zone grain size for parent metal thickness of 0.15 mm, 0.2 mm, 0.25 mm & 0.3 mm respectively. As the grains in some parts of the weld fusion zone are elongated, an average value was reported by measuring grain size at different locations in the fusion zone of each sample. The measured grain sizes are presented in Table.5

Table.5 Measured grain sizes

Thickness (mm)	0.15	0.20	0.25	0.3
Grain Size (Microns)	24.327	29.794	30.861	43.916

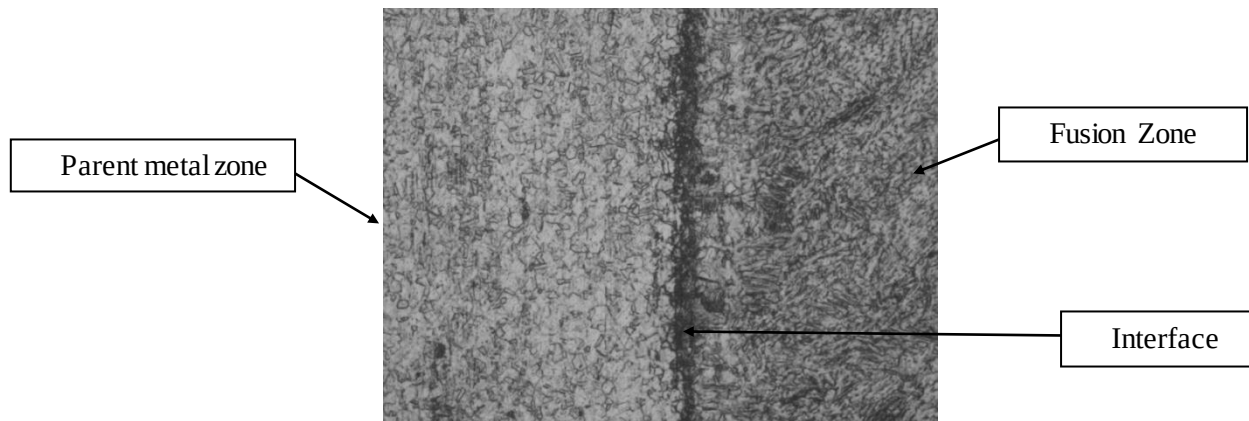


Figure.3 Microstructure of welded joint

From Figure 3, it is understood that the weldments consist of a columnar dendritic structure. A pronounced acicular δ -ferrite formation (dark etching) is observed around the cellular dendritic austenitic grain.

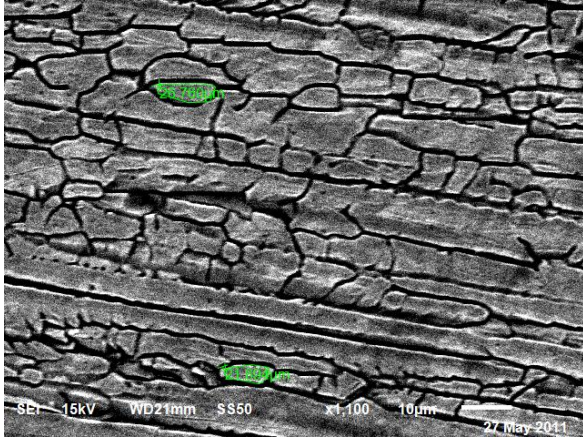


Fig.4a Grain size at 0.15 mm thick

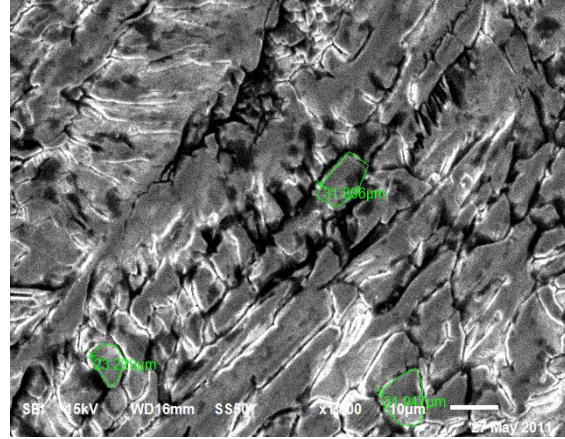


Fig.4b Grain size at 0.20 mm thick

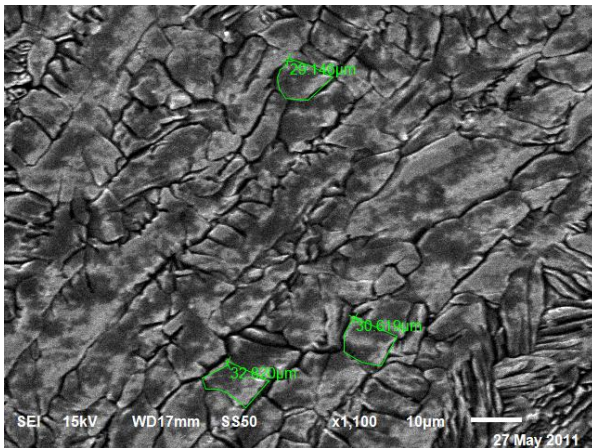


Fig.4c Grain size at 0.25 mm thick

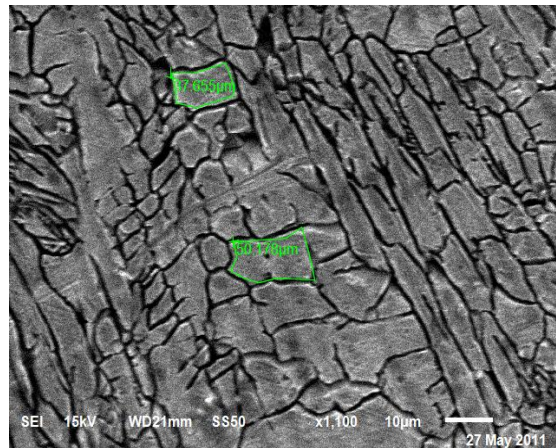


Fig.4d Grain size at 0.30 mm thick

The fine grains observed in the fusion zone due to optimum heat input may be responsible for the better grain size of these welded joints. The finer grain size of fusion zone is responsible for the increase in strength of the welded joints.

2.3. Measurement of Vickers Micro Hardness

Vickers Micro hardness was done as per ASTM E384. The samples were cut in transverse direction from the welded specimens and Vickers Micro Hardness values across the weld joint at an interval of 0.3

mm using Digital Micro Hardness testing Machine, make METSUZAWA CO LTD, JAPAN, Model No: MMT-X7 and are presented in Table.5

Table 5 Variation of hardness values across the weld joint at 0.3 mm interval

Parent metal thickness (mm)	Hardness values in VHN at different locations on the weld joint								
	HAZ zone		Fusion zone					HAZ zone	
	1	2	3	4	5	6	7	8	9
0.15	176.2	180.2	205.2	194.5	210.4	208.3	197.3	184.2	180.0
0.20	175.9	179.8	210.2	206.5	207.2	205.1	194.6	197.4	192.7
0.25	203.9	216.9	216	200.6	202.5	206.8	213.4	206.3	193.9
0.30	172.9	175.8	218.9	203.5	218.7	217.9	215.1	210.1	208.2

In the Table.5 points 1,2,8,9 indicates at Heat Affected Zone (HAZ) and the points 3, 4,5,6,7 indicates at Fusion Zone (FZ). The location of the hardness measuring points is shown in Figure.5. The variation of hardness across the weld is shown in Figure.6.

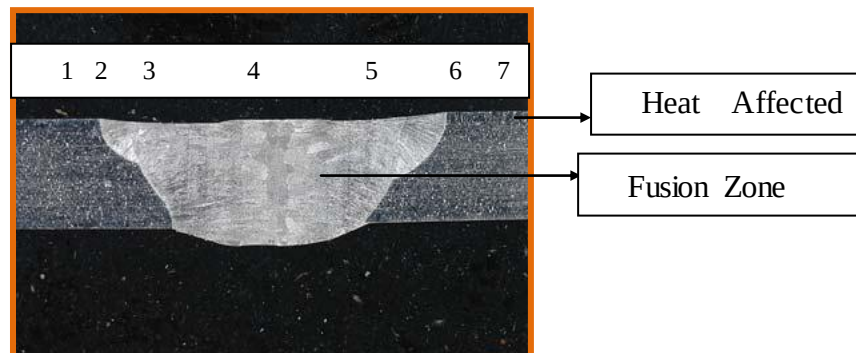


Fig.5 Location of hardness measuring points on the weld joint

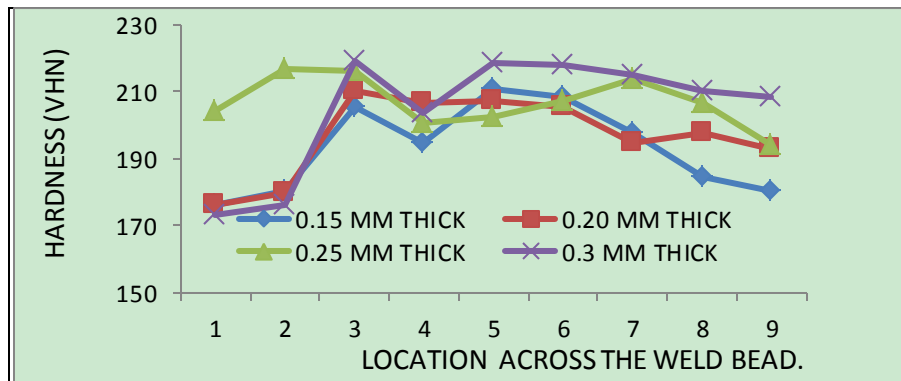


Fig.6 Variation of hardness across the weld

From Table 5 and Figure 6 it is understood that hardness at FZ is more and keeps on decreasing towards HAZ.

According to Hall & Pitch equation grain size and hardness are inversely proportional. As the grain size of FZ keeps on increasing with parent metal thickness, hardness of FZ keeps on decreasing. The variation of hardness with thickness is shown in Figure 7 and the values are tabulated in Table.

Table.6 Measured hardness values

Thickness (mm)	0.15	0.20	0.25	0.3
Hardness(VHN)	214.82	207.86	204.72	203.14

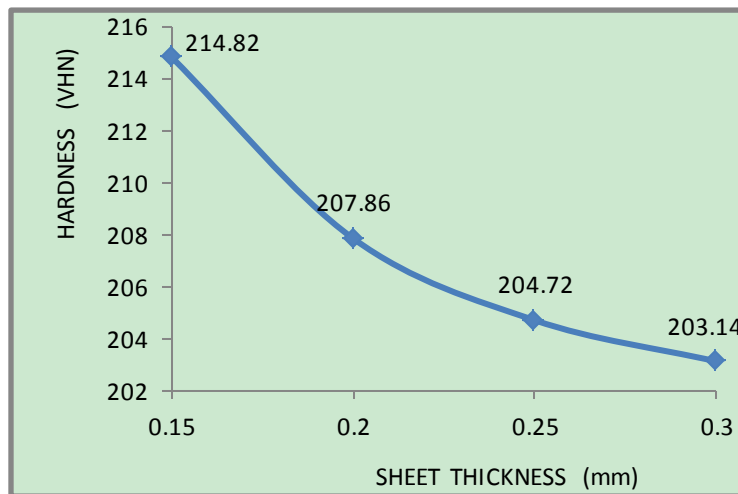


Fig.7 Variation of fusion zone hardness

2.4. Measurement of ultimate tensile strength

Three transverse tensile specimens are prepared as per ASTM E8M-04 guidelines and the specimens after wire cut Electro Discharge Machining are shown in Figure 7. Tensile tests are carried out in 100kN computer controlled Universal Testing Machine (ZENON, Model No: WDW-100). The specimen is loaded at a rate of 1.5 KN/min as per ASTM specifications, so that the tensile specimens undergo deformation. From the stress strain curve, the yield and ultimate tensile strength of the weld joints is evaluated and the average of three results is presented in Table 7.

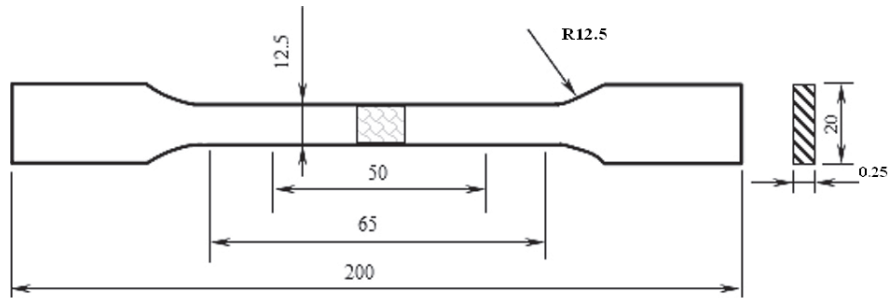


Figure. 7 Schematic diagram of tensile specimen as per ASTM E8.

Table.7 Measured hardness values

Thickness (mm)	0.15	0.20	0.25	0.3
Ultimate Tensile Strength (MPa)	692	699	708	683

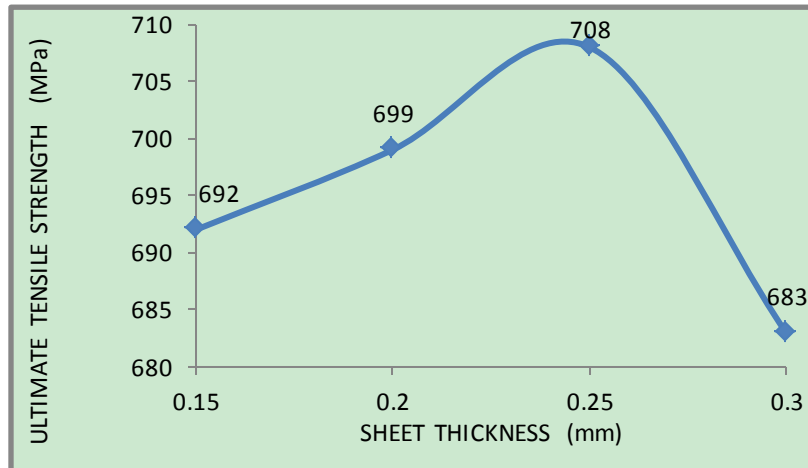


Fig.9 Variation of ultimate tensile strength

From Figure 8, it is understood that the ultimate tensile strength keeps on increasing with thickness of parent metal up to a thickness of 0.25 mm. At 0.3 mm thickness there is a sudden decrease in the ultimate tensile strength is due to improper fusion of the parent metal.

The tensile specimens before and after testing are shown in Figures 10 and 11. Sample of 0.20 mm and 0.25 mm thick, failed at HAZ, because the weakest section of the weld joint is Heat Affected Zone (HAZ). Sample of thick 0.3 mm failed at Fusion Zone (FZ) because the peak current used for joining this sample is very low of 7 Amperes. This is because of improper fusing of base metal. Sample of thickness 0.15 mm failed at interface between FZ and HAZ. This is because of formation of martensite which is hard and brittle. Also for 0.15 mm thick over melting of base metal had taken place.



Figure 10. Tensile specimens before testing

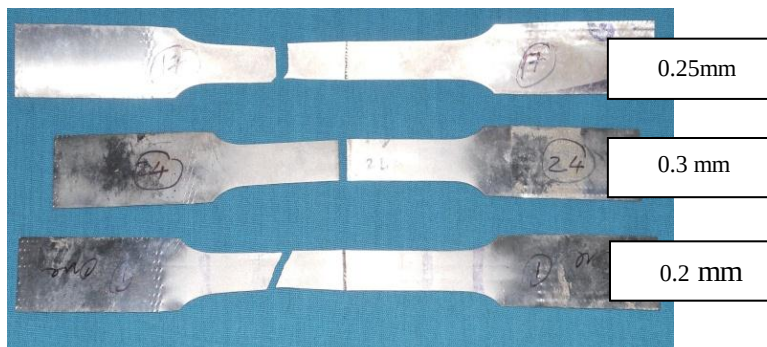


Figure 11. Tensile specimens after testing

3. CONCLUSIONS

The following conclusions are drawn from the experiments performed on various thickness of AISI 304L sheets.

1. For same welding conditions, the weld bead geometry dimensions are poor for 0.30 mm thick, as the peak current applied is not sufficient to fuse the base metal completely. Also for 0.15 mm thick over melting of base current was noticed because of higher peak current.
2. For same welding conditions, for all the thickness of base metal, the variation of microstructure is almost same. However there is some variation in grain size was noticed. Smaller fine and smaller size grains are observed in 0.25 mm thick and this is one of the reasons for higher hardness and ultimate tensile strength.
3. The ultimate tensile strength of the weld joint increases from 0.15 mm thick to 0.25 mm thick and there after decreases because of improper fusion of the parent metal.
4. It is revealed from the experiments performed, that for the given welding conditions of (peak current of 7 Amperes, back current of 4 Amperes, pulse rate of 40 pulses /second and pulse width of 50%) , 0.25 mm thick AISI 304L sheets has optimal weld quality characteristics.

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