

# Intermetallic compounds

## 4 - 1 – Synthesis and thermoelectric properties of polycrystalline $Zn_4Sb_3$ compounds prepared by hot pressing method

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Single phase  $\beta - Zn_4Sb_3$  samples were prepared by using hot pressing method. Their structural and morphological properties were studied by x-ray diffraction analysis (XRD) and Scanning Electron Microscopy (SEM), respectively. The transport properties were evaluated from Seebeck coefficient  $S(T)$  and electrical resistivity  $\rho(T)$  measurements in the temperature range between 100 and 290K.  $S(T)$  shows positive values suggesting a p-type material, its magnitude increases with the processing time, reaching maximum values close to 300  $\mu V/K$ . The electrical resistivity, measured by four D.C. probe method, increases with processing time, however its magnitude is less than 25  $m\Omega\cdot cm$ . An order-disorder transition was observed in the transport properties around 240K, which is a characteristic property of pure single crystals of  $\beta - Zn_4Sb_3$ . From  $S(T)$  and  $\rho(T)$  experimental data the thermoelectric power factor PF was calculated, this performance parameter reaches maximum values close to 100  $\mu W/K^2\cdot cm$ , which make this kind of compounds promising materials for thermoelectric applications.

## 4 - 2 – Metallic cathode surface modification by using low pressure pulsed vacuum arc discharge

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Electrical discharges in a pulsed vacuum arc system at low pressure were produced, using a peak current of 100 A with pulses of 30 ms. Discharges were carried out applying a voltage of 104 V between the electrodes. Materials used as cathode were Ti, Zr, Ni, Cu, Mo and W. The cathodes morphology after the discharges production was studied by using the scanning electron microscopy (SEM) technique. Ti and Zr presented the highest erosion. Moreover, circular craters on Ni and Mo cathodes were observed and a region of the Zr cathode, with high erosion and great quantity of craters was analyzed. The discharge voltage for each material was measured, obtaining arc voltage values. Finally, relationships between arc voltages and

some material characteristics as melting point, boiling point, electrical and thermal conductivity were observed.

Keywords: Morphology, Spots, Arc voltage, Metallic cathodes.

## 4 - 3 – Microstructural evolution in TiZrN thin films varying the substrate temperature during deposition

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Materials microstructure is considered as one of the most relevant characteristics for defining their performance and specific applications. For this reason, the microstructure becomes an important factor in material science. In this work the development of the microstructure as a function of substrate temperature in Titanium-Zirconium Nitride thin films is studied. The films were grown by the cathodic pulsed vacuum arc technique on stainless steel 316L substrates varying the temperature values of 20, 50, 100, 150 and 200°C. For the films growth, four pulses were applied; each 30 ms and time between these pulses was 40 s. X-ray diffraction was used to identify the crystallographic phase present in the films evaluating the lattice parameter. By using Scherrer equation, microstructure characterization was carried out depending on the lattice strain and crystallite size analyzing the influence of the substrate temperature. Other important measurement for elucidating important films structure characteristics were rocking curves in order to obtain the dislocations density in the material, presenting a substantial broadening and asymmetry. Surface analysis was carried out by scanning probe microscopy in atomic force microscope mode, obtaining values for roughness and grain size depending on the parameter substrate temperature.

#### 4 - 4 – Effect of annealing process on TiN/TiC bilayers grown by pulsed arc discharge

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In this work, a study of annealing process effect on TiN/TiC bilayer is presented. The annealing temperature was varied between 0 and 500 °C. The materials were produced by plasma-assisted pulsed arc discharge. In order to grow the films, a target of Ti with 99.9999 purity and stainless-steel 304 substrate were used. For the production of TiN layer, the reaction chamber was filled up with nitrogen gas until reaching a 2.5 mbar and the discharge was performed at 310 V. The TiC layer was grown in a methane atmosphere at 3.0 mbar and 270 V. Both films were grown at a substrate temperature of 150 °C. The microstructure evolution was study by means of XRD. At 400 °C, TiO<sub>2</sub> phase begun to appear and it was well observed at 500 °C. Crystallite size and microstrain was obtained as a function of the annealing temperature. XPS technique was employed for analyzing the bilayers before and after the annealing process. Narrow spectra of Ti2p, N1s and O1s were obtained, presenting TiO phases.

#### 4 - 5 – Study of Cohesive, Electronic, and Magnetic Properties of the Ni-In Intermetallic System

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Cohesive, electronic and magnetic properties of the intermetallic system Ni-In, specifically the stable phases Ni<sub>3</sub>In-hP8, Ni<sub>2</sub>In-hP6, NiIn-hP6 y Ni<sub>2</sub>In<sub>3</sub>-hP5, have been investigated. Presently, these materials are of great interest in connection to the application of the In-Sn alloys as lead-free micro-soldering alloys, and considering Ni as the contact material. In spite of this, scarce literature regarding basic thermodynamic properties of the Ni-In intermetallic phases has been found. Full-Potential Linear Augmented Plane Wave method (FP-LAPW) within the framework of the Density Functional Theory (DFT) with exchange and correlation effects in the Generalized Gradient (GGA) and Local Density (LDA) approximations is used. All

calculations include spin polarization. Structural parameters, formation energies and cohesive properties of different phases are studied through minimization of internal parameters. Density of states (DOS) is analyzed for each optimized structure. We found that the NiIn-hP6 phase is the most stable one and only the Ni<sub>3</sub>In-hP8 phase exhibits magnetic properties.

#### 4 - 6 – (Fe, Si)<sub>2</sub>Mo Laves phase solid solution

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Silicon plays an outstanding role in C14 Laves phase Fe<sub>2</sub>Mo stability. However, only a few early works have been devoted to study silicon solubility. Experimental studies established the existence of C14 phase at three compositions in the ternary system Fe–Mo–Si along a constant 0.66 at %Mo content. A semi empirical approach to describe phases stabilities in the ternary system was recently enhanced by the incorporation to the data base of FeSiMo formation energy calculated with first principles methods. Some of the authors of the present work have presented in a previous paper the first fully first principles calculation of the ground state and thermodynamic functions at finite temperatures of the pseudo binary system Fe<sub>2</sub>Mo – Si<sub>2</sub>Mo. A cluster expansion based on first principles calculation of formation energies and Monte Carlo simulations for finite temperatures have been implemented. A miscibility gap that had not been experimentally reported has been predicted. We present in this work a different approach to random (Fe, Si)<sub>2</sub>Mo solid solution by means of special quasirandom structures (sqs) as a proven technique to simulate random alloys. The ATAT package was used to generate sqs and the SIESTA code based on pseudo potentials was used to calculate formation energies. The previous results were confirmed.

#### 4 - 7 – Density Functional Theory applied to study of the chemical reactivity of Mg and Mg<sub>2</sub>Ni alloy

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Hydrogen is an excellent energy carrier to be used in both fuel cells and combustion engines as a clean fuel. However, the success of a hydrogen economy relies on our ability to store hydrogen safely and economically under ambient conditions and with large gravimetric and volumetric density. Magnesium-based alloys are considered to be the most promising materials for hydrogen storage because of their high storage capacity, the abundance of magnesium in the Earth's crust and low cost compared to alternative systems. Of all the magnesium-based alloys, the intermetallic compound Mg<sub>2</sub>Ni can be easily synthesized and it reacts readily with gaseous hydrogen to form reversibly the stable hydride Mg<sub>2</sub>NiH<sub>4</sub>, which, from the engineering point of view, is considered to be a very convenient material for hydrogen storage purposes. Using a density functional approach calculation, the energetic, electronic and reactivity properties of Mg and Mg<sub>2</sub>Ni alloy are systematically investigated. Our results indicate that pure magnesium is more reactive than Mg<sub>2</sub>Ni alloy against hydrogen adsorption and the molecular electrostatic potentials show us the sites most susceptible to electrophilic attack.

#### 4 - 8 – Electrical resistivity of pressurized iron and Fe-Ru alloys

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The  $p - T$  phase diagram of iron is complex, displaying at least four solid phases with different magnetic properties. Hexagonal iron is the stable phase above 13 GPa and its magnetic state, thought to be antiferromagnetic, is still the object of debate. Notably, between 13 GPa and 31 GPa an unconventional superconducting state develops.

Iron-ruthenium alloys, Fe<sub>1-x</sub>Ru<sub>x</sub>, have a hexagonal structure for  $x > 0.3$ . The magnetic ground state of these alloys is also under debate, and superconductivity has been reported only for very low Fe-content (i.e.,  $x \sim 1$ ). We will discuss differences and similarities of the pressure- and alloying-induced hexagonal phases of iron as probed by low temperature electrical resistivity measurements.

#### 4 - 9 – Atomistic modeling of ternary additions to NiTi and quaternary additions to NiTiPd, NiTiPt and NiTiHf shape memory alloys

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Development of new NiTi-based high temperature shape memory alloys (SMA) relies mainly on the ability to identify the appropriate alloying additions that introduce the desired changes in the austenite-martensite transition temperature. Experimental work has been done in this direction, and several elements have been studied that have that effect but, as is often the case in alloy development programs, ternary or higher order additions introduce changes in properties, some of them critical enough to invalidate their use for specific applications. It is also common that a variety of practical considerations, such as costs, processing, environmental effect, and others, introduce additional difficulties, making the search of the appropriate candidates a lengthy and costly process. In spite of the enormous progress and the inherent difficulties of performing systematic studies of new compositions, no single picture has emerged yet to systematically deal with the different variables that should be taken into account for any given application. This is the case with ternary additions such as Pd, Pt and Au, in alloys Ti<sub>50</sub>Ni<sub>50-x</sub>Y<sub>x</sub> (Y = Pd, Pt, Hf), which are among the most promising candidates for high temperature shape memory alloys (HTSMA), but due to the costs associated with precious metals, other alternatives must be considered. In addition, while several studies can be cited on specific ternary systems, basic information on the quaternary cases is, in comparison, lacking. Modeling focusing on the basic properties of large numbers of ternary and quaternary cases could then be helpful in the process of downselecting compositions that meet desired criteria in terms of strength, density, phase structure, etc. As a first step in this direction, this work provides a systematic study of a large number of additions to NiTi, some known and some never tried before: X = Au, Pt, Ir, Os, Re, W, Ta, Hf, Ag, Pd, Rh, Ru, Tc, Mo, Nb, Zr, Zn, Cu, Co, Fe, Mn, V, Sc, Si, Al and Mg. In addition, we extend this work to the study of the physical properties of quaternary alloys Ni-Ti-Pd-X, Ni-Ti-Pt-X and Ni-Ti-Hf-X, with the same options for X, and compare their changes relative to the ternary base alloy. The atomistic modeling work is made using the Bozzolo-Ferrante-Smith (BFS) method for alloys for the energetics. Bulk properties such as lattice parameter, energy of formation, and bulk modulus of the B2 alloys are studied for variations due to the presence of one or more additives, thus developing a database for

HTSMA candidates that could aid in current and future experimental work towards the development of HTSMA for specific applications.

#### 4 - 10 – Investigation on the oscillatory behaviour of the lattice parameter in ternary iron-nitrogen compounds

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In the last years, many theoretical and experimental studies have been reported on TM-Fe<sub>3</sub>N alloys (TM, 3d transition metal), due to the potential technological applications on derivatives of Fe<sub>4</sub>N in very important magnetic properties, ie. high density magnetic recording. These compounds have a perovskite-type structure, where the TM atom is located at the corner of the cube, the Fe atom in the center of the faces and the N atom in the center of the cube, corresponding to the 1a, 3c and 1b Wyckoff position, respectively. In the present work, using ab-initio calculations (Wien2k code), we show that the lattice parameter have an oscillatory behaviour. The oscillations of these parameters are decreasing with increasing of the atomic number Z of the TM-Fe<sub>3</sub>N compound. The oscillations of the lattice parameter are strongly related with the type of TM in the compound and the charge distribution of the d-orbitals of the atoms in the sites 1a (TM) and 3c (Fe). The magnetic properties of compound changes with the 3d metal, i.e., it is non magnetic for TM=Sc, ferrimagnetic for TM=Ti, V and Cr, and ferromagnetic for TM= Mn, Fe, Co, Ni, Cu and Zn, in the case of Cu and Zn the ferromagnetism is due only to the Fe atoms in 3c sites. It is worth to mention that some authors do not consider Zn in the 3d series; in the present work we have included it in our series for completeness.

#### 4 - 11 – A first-principles study of hydrogen storage in saline hydrides. Lithium hydride series.

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The problem in extending the application of hydrogen as a clean energy source is based on storage and portability. In this regard, saline hydrides such as lithium hydride appear as new alternatives to this, owing to their properties, their high reactivity and reversibility. In addition to experimental studies, theoretical research can provide extensive information about these types of systems. The first principles calculations based on density functional theory

(DFT) have been used to study the physical properties of Li-H compounds. The crystal structure, electronic properties and internal optimization parameters are treated by the LAPW method implemented in the WIEN2k code. In the present study we show the comparison of two different phases of lithium hydride compounds, in four different crystal structures, with the purpose of comparing the formation energies in all cases, and determine which is the structure with the best structural properties for applications in energy reservoir. The comparisons between the results obtained in the structures of lithium-hydride are discussed in this work.

#### 4 - 12 – Ab-initio modeling of phase stability and thermodynamic properties of Cu-In and Cu-Sn intermetallics. Calculation of energy parameters involved in the thermodynamic assessment of the Cu-In-Sn system using sublattice models

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The In-48at.%Sn eutectic alloy is an attractive candidate for the development of Pb-free solders within the diffusion soldering method. In order to understand the phase formation between the soldering alloy and the Cu substrate, the knowledge of the physico-chemical properties of the formed intermetallic phases (IPs) and the phase equilibrium properties of the Cu-In-Sn system are of great importance. Previous attempts to investigate the phase stability of the IPs of the Cu-In-Sn system were based on combining the experimental information available, with thermodynamic models for the Gibbs free energy of the ternary and binaries phases. In this way using methods like the CALPHAD method ("Calculation of Phase Diagrams") it is possible to get useful predictions for the phase relations on the ternary field, starting from information of the binary subsystems. Extensions of the binary phases to the ternary field can be modeled by the Compound Energy Formalism, in which varying amounts of the third element are added substitutionally to the binary phase. Certain IPs of the Cu-In-Sn system can be treated with models of the type (Cu)<sub>a</sub>(In,Sn)<sub>b</sub>, while others non-stoichiometric Cu-In and Cu-Sn binary phases, with models of the type (Cu)<sub>a</sub>(In,Sn)<sub>b</sub>(In)<sub>c</sub> o (Cu)<sub>a</sub>(In,Sn)<sub>b</sub>(Sn)<sub>c</sub>, respectively. In this work we perform *ab-initio* calculations

using the Vasp Code to determine the energy parameters involved in the application of CEF to various IPs of the Cu-In-Sn system. We use the projector augmented wave potentials (PAW) and the exchange-correlation functions of Perdew and Wang in the generalized gradient approximation. We study the end-member compounds involved in the CEF treatment of the ternary phases generated by adding In to the binaries  $\epsilon$ -Cu<sub>3</sub>Sn (oP8) and  $\xi$ -Cu<sub>10</sub>Sn<sub>3</sub> (hP26), and adding Sn to the CuIn<sub>2</sub> phase (tI12). This work extends a recent research performed for the end members associated to  $\delta$ -Cu<sub>7</sub>In<sub>3</sub> (aP40),  $\eta$ -Cu<sub>2</sub>In (hP6) and  $\eta$ -Cu<sub>6</sub>Sn<sub>5</sub> (mC44) phases. All these results are considered to establish trends in the relative stability and thermodynamic properties of the IPs of the Cu-In and Cu-Sn subsystems. We critically compare the calculated formation energies for the CEFs compounds with data previously obtained by phenomenological Cu-In-Sn CALPHAD analysis.