THE GREAT WORLD OF NANOTECHNOLOGY

Marcos Augusto de Lima Nobre

(Organizador)

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APRESENTAÇÃO

O mundo em escala dos nanômetros tem-se mostrado cada vez mais presente no cotidiano. Em qualquer área encaixamos o nano, e muitas palavras têm sido criadas com o prefixo nano. Algo que exiba uma de suas dimensões na escala de um bilionésimo de metro pertence a este universo, que de forma gradual tem alcançado a ciência e a tecnologia. A nanociência e nanotecnologia têm modificado tintas, tecidos, metais, cerâmicas, polímeros a compreensão dos minérios e minerais, por fim criando a necessidade de cursos para otimizar a compreensão de seus conceitos aplicados a engenharia, a medicina e áreas correlatas. O mundo dos “nano” tem alcançado as ligas metálicas, os argilominerais, o ensino aplicado, a mecânicas dos fluidos e pós cerâmicos funcionais com partículas com tão baixa densidade que podem ser consideradas apenas casca. Cada um destes tópicos está sendo desenvolvido neste exato momento para ganharmos durabilidade, novos materiais mais fortes, mas com menos peso, novas técnicas de ensino para conceitos novos e inovadores, transporte mais eficiente de combustíveis e biocombustíveis em linhas e dutos cada vez menores e pós nanométricos funcionais capazes de acelerar reações químicas. Este livro traz um conjunto de textos abordando diversos aspectos dos conceitos materiais em escala dos nanômetros.

Desejo a todos uma excelente leitura!!

Marcos Augusto de Lima Nobre

SUMÁRIO

CAPÍTULO 1

PRODUÇÃO E CARACTERIZAÇÃO DO COMPOSTO INTERMETÁLICO TERMOELÉTRICO TiNiSn

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RESUMO: Uma liga intermetálica dotada de propriedades termoelétricas foi sintetizada por Mechanical Alloying. Os pós elementares de alta pureza de Ti, Ni e Sn na composição de TiNiSn (uma liga Half Heusler) foram moídos por 4 horas. A evolução estrutural do material foi estudada por medidas de Difração de Raio X (DRX) e refinamentos de parâmetros estruturais pelo método de Rietveld. A estabilidade térmica do material foi investigada a partir de Calorimetria Diferencial de Varredura (CDV). Baseado no termograma da calorimetria, a amostra foi recozida nas temperaturas de 310˚C e 380˚C, seguido de resfriamento a ar. Após o recozimento, constatou-se a observação de duas novas fases.

PALAVRAS-CHAVE: Mechanical Alloying, Moagem De Alta Energia, Termoelétrico, Half-Heusler, Intermetálico

PRODUCTION AND CHARACTERIZATION OF THE INTERMETALLIC THERMOELECTRIC COMPOUND TiNiSn

ABSTRACT: An intermetallic alloy with thermoelectric properties was synthesized through Mechanical Alloying. The high purity elemental powders of Ti, Ni and Sn at the composition of TiNiSn (a Half Heusler Alloy) was milled for 4 hours. The structural evolution was studied through X-Ray Diffraction measurements and refinement o f s tructural p arameters using the Rietveld method. The thermal stability of the material was investigated through Differential Scanning Calorimetry. Based on the thermal chart obtained by the DSC measurement, the sample was annealed at the temperatures of 310˚C e 380˚C, followed by air cooling. After the annealing, new phases were observed.

KEYWORDS: Mechanical Alloying; High Energy Ball Milling; Thermoelectric; Half Heusler; Intermetallic

1 . INTRODUCTION

As world population increases, the use of energy sources to supply society's demands increases as well, regardless of whether they are renewable or not, which leads to one of biggest problems of mankind: the search for renewable low-cost energy sources and ways of optimizing it. Recovery techniques have been developed for use on generators [2].

The search for thermoelectric materials are inserted in this context, on the broad spectrum of techniques and process developments towards energy harvesting; the operation of these materials consists on the physical principles of the Thermoelectric Effects (Seebeck Effect), which generates a tension from the migration of charge carriers on a temperature gradient; the guidance as a rule of thumb is from the higher energy part of the system towards the lower (from the hotter side to the cold) [7]. Such effects allow the direct conversion of electric energy to thermal energy and vice-versa; materials with this property are use on microelectronic components as well as the energy industry for harvesting energy waste.

The performance of thermoelectric materials is equated by the Figure of Merit (*ZT*), defined as: $\mathbf{ZT = (S^2\sigma T/\kappa)}$, where **S, σ, k e T** represents respectively the Seebeck Coefficient, Electrical Conductivity, Thermal Conductivity (considering both contribution of the lattice and of the charge carriers) and Absolute Temperature (et al Yang Jiong). State of the art thermoelectric materials have intrinsic high conductivity, Seebeck Coefficient modulus and low thermal conductivity [9].

The bigger part on enhancing thermoelectric materials lies on the reduction of lattice thermal conductivity through the insertion of punctual defects in the atomic interstices and grain size reduction, as well as increase of interfaces or grain boundaries of the compound; high thermal conductivity of metallic alloys is the main reason for the limited application of such materials and their performance [3]. In order to make the application of metallic alloys viable on thermoelectric material, High Energy Ball Milling becomes the most effective processment, due to simplicity and low cost.

Several materials are studied for the application on thermoelectric semiconductor materials; however, one specific class of intermetallic compounds stands out from the others, being defined as Half Heusler. Specifically, these compounds have a 1:1:1 stoichiometry, where the number of electronic vacancies of the material's crystalline structure will directly influence on its optical and thermal properties. Structurally, they resemble to the structure of SiO_2 and of semiconductors as GaAs, showing a similar structure to NaCl [10].

Half Heusler compounds of composition MNiSn (M = Ti, Zr, Hf) show promising thermoelectric properties due to a narrow gap, of around to 0,1-0,2 eV on the Fermi energy level. However, it is found to have great difficulty during processment in order

to achieve nucleation of the material (generally made by arc melting), often resulting in compositional segregation, which can be worked around through the annealing of the material for long durations, despite the formation of highly dense and coarse grain [5].

Welding, fracture and rewelding of particles on High Energy Ball Milling results on the creation of nanostructured materials on room temperature in solid state [8]. From this processment, nanometric order materials are obtained, with reduced grain size, as well as a higher number of interfacial defects, in such a way that thermal conductivity can be reduced to enhance the Power Factor of the Figure of Merit.

A material with the same characteristics as the ones made by wet chemical processes (precursor materials are dispersed or dissolved on solvents and then precipitate through manipulation of the media's Ph) can be obtained. Comparatively, materials with less defects are obtained through wet chemical process than high energy ball milling (which would lead to a higher charge mobility). However, practical results were the opposite; materials produced by high energy ball milling show higher charge mobility. The reason for this phenomenon according to scientists is that the surfaces of the crystal o wet chemical processes get covered by chemical stabilization agents, resulting on the displacement of atomic defects towards the grain boundary [1].

Studies show that the addition of Ni atoms to the alloy TiNiSn might increase the Figure of Merit ***ZT*** from the creation of secondary Full Heusler ($TiNi_2Sn$) phases. The so called phase densification promotes the phonic dispersion on the phase $TiNi_2Sn$, resulting on the reduction crystalline thermal conductivity, at the concentrations of 30% of Full Heusler phase and 5% of Half Heusler phase; the alloy's electrical conductivity might be increased by the addition of metallic phases to the microstructure, which contributes with electrons, reducing electric resistivity [6].

Materials characterization can be made in several ways, such as Raman Spectroscopy, X Ray Fluorescence Spectroscopy, Photoacoustic Absorption Spectroscopy, X Ray Diffraction and Absorption. However, when it comes to analyzing a particulate material, X Ray Diffraction becomes the most practical and effective technique, not being a complex operational process in order to complete the analysis. This technique in question is used for determining structural profiles of amorphous and crystalline materials, obtaining information such as special group, lattice parameters, atomic positions in the unit cell, microdeformation, coordination number. The diffraction phenomenon in the material happens whenever the wave length λ is of the same magnitude of the distance between the scattering centers in the center of the crystal. The entire phenomenon comprises of the scattering of the constructive and destructive rays.

With the obtained data after the XRD measurements, simulations can be made to gather data regarding the structure of a material after a processment that alters its physical-chemical nature (in this case High Energy Ball Milling), through

refinements and adjustments starting from theoretical models (Rietveld Method). It is also possible to make quantitative definitions referent to the phases that make up the material, besides determining preferred atomic orientations, mean size and crystallite microdeformation [4, 11, 12].

2 . MATERIALS AND METHODS

The synthesis of the material consisted on the following steps:

- Preparation of the TiNiSn compound

The compound was synthesized through Mechanical Alloying on a SPEX type high energy ball mill, according to the following order. High purity titanium, nickel and tin were weighed stoichiometrically in order to achieve TiNiSn. Then the powder mixture was place inside the milling vessel, with steel balls which were the milling bodies for the process. The selected BPR was 5:1.

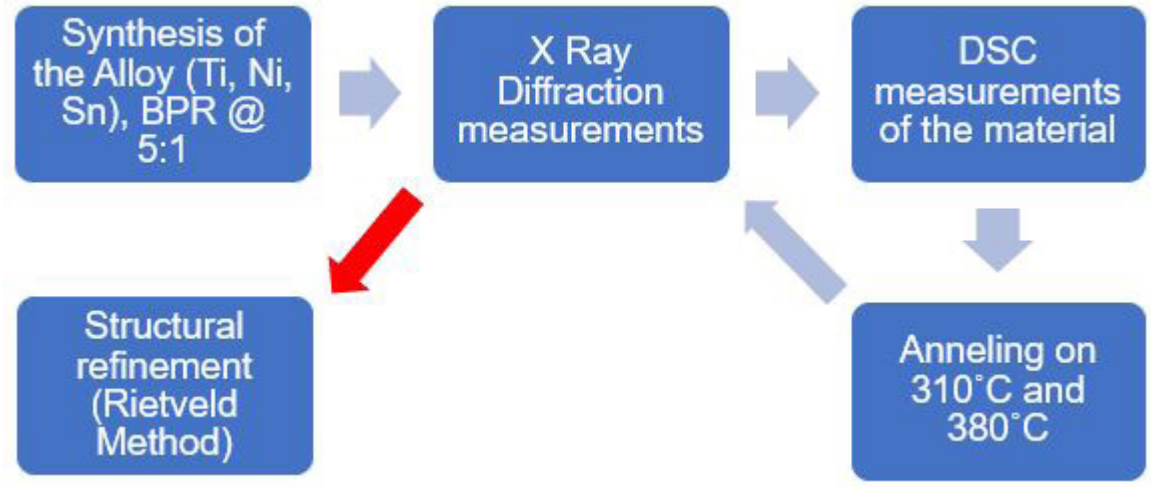
The vessel was closed with argon gas atmosphere in order to prevent oxidation. Then the vessel in question was placed into the mill for the processment of 1 hour. After this time, a small amount of the powder mixture was removed from the vessel and characterized through XRD (X-Ray Diffraction) measurements. When the formation of the desired compound was observed, the sample was stored separately. In case the compound wasn't observed, the powder was returned to the vessel, which was subjected to further milling for 1 hour. The proceeding was repeated until a completely pure compound was obtained.

- Alloy characterization

The characterization of the obtained compound was made using the following techniques:

1. Measurements of the XRD patterns, that allowed the identification of the formed phases in the material, with the support of databases such as ICSD. All XRD measurements were made on a Panalyical Empyrean diffractometer.
2. Simulations of the XRD patterns using the Rietveld method, which determines precisely the relevant structural parameter values for the present phases in the material, such as lattice parameter, crystallite size, preferential orientations, structural strain. This data was obtained through refinements using the software GSAS (General Structure Analysis System).
3. Differential Scanning Calorimetry to evaluate thermal stability, allowing the determination of temperatures where changes to the structure of the material happens, such as structural relaxation, crystallization of amorphous phases, enthalpy variation, specific heat calculations, formation kinetics.

Figura 1: Synthesis route of the TiNiSn thermoelectric compound



3 . RESULTS AND DISCUSSION

From the sample milled periodically each one hour, it's X-Ray Diffraction pattern was obtained, corresponding to each milling hour, from 1 to 4 hours, to then, analyze the variations between the diffractographic profiles, corresponding to each hour of processment, followed by the structural determination of the sample containing the desired phase, in this case, the sample that had the formed TiNiSn phase.

Using the software PANalytical X'Pert HighScore Plus, it was possible to identify that the in the sample milled for 3 hours, are phases of TiNiSn (Nº PDF 03-065-0617), NiTi (Nº PDF 03-065-5537) and TiNi2Sn (Nº PDF 00-052-0905), while that in the sample milled for 4 hours there are only TiNiSn and NiTi phases.

For the simulations of the material's XRD profiles through the Rietveld method using the GSAS software, the samples milled for 4 hours, annealed at the temperatures of 310˚C and 380˚C were selected (because the DSC measurement showed exothermic events at these temperatures, which could indicate phase nucleation, thus it was interesting to evaluate those events, as seen on Figure 2; the measurement in question was conducted on a heating ramp from 100˚C to 500˚C). The phases in question and its ICSD number are displayed on tables 1 and 2.

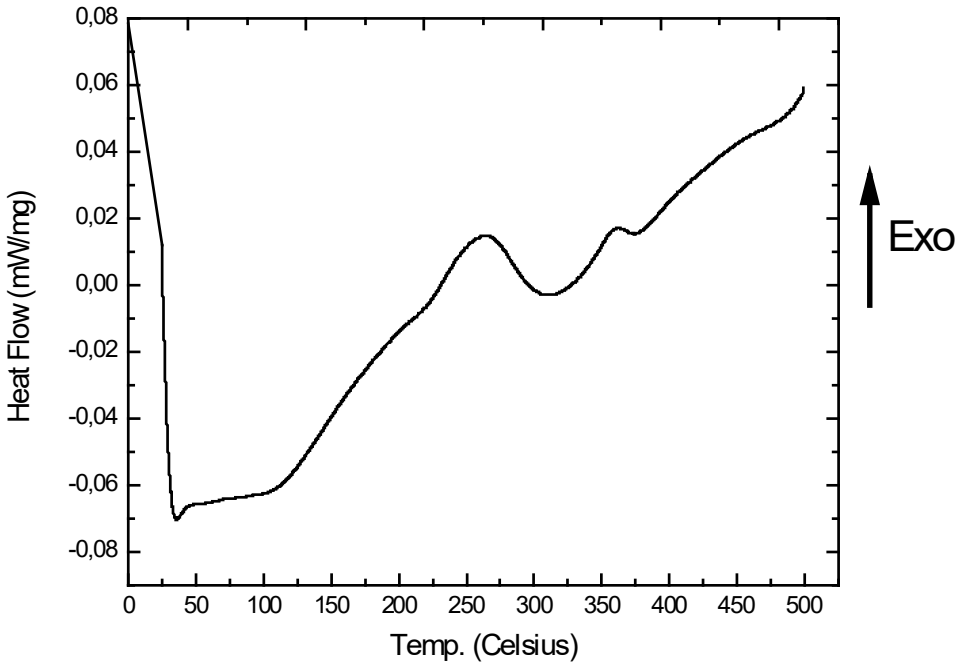
Table 1: Present phases on the powder sample milled for 4 hours and annealed at 310˚C

Phase	CIF
TiNiSn	657175
Ni_3Sn_4	105363

Table 2: Present phases on the powder sample milled for 4 hours and annealed at 380˚C

Phase	CIF
TiNiSn	657175
$Ni_{3.39}Sn_4$	105362

Figure 2: DSC measurement of the milled powder



Source: Created by the author

From the simulations of the diffractographic profiles, through the Rietveld method, an expected diffractogram for the synthesized materials was obtained.

Figure 3: XRD measurement of the sample milled for 4 hours and annealed at 310˚C

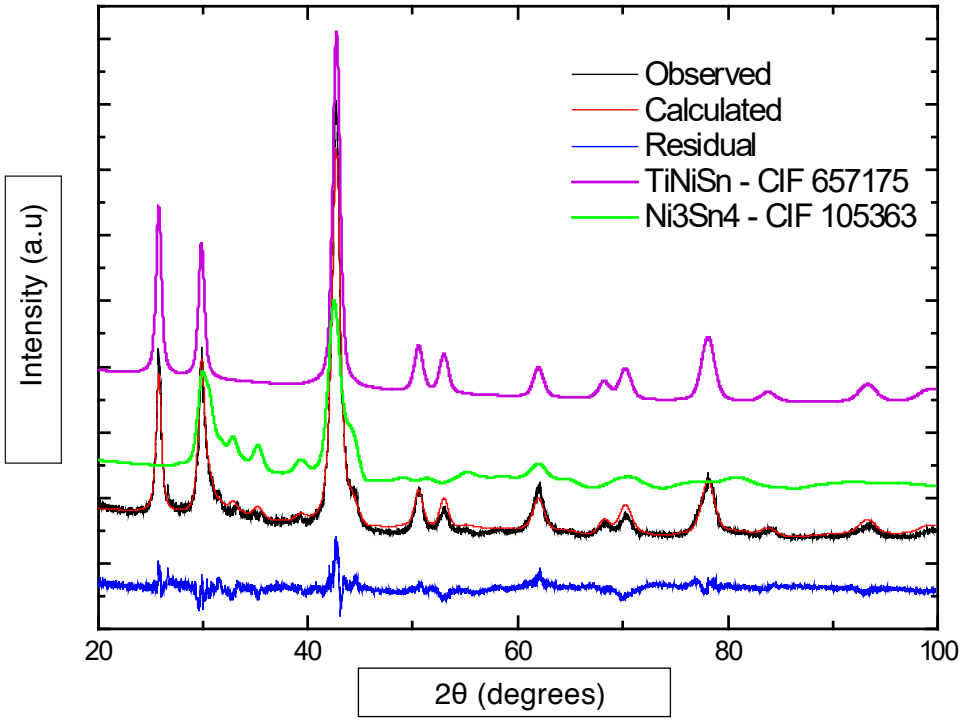


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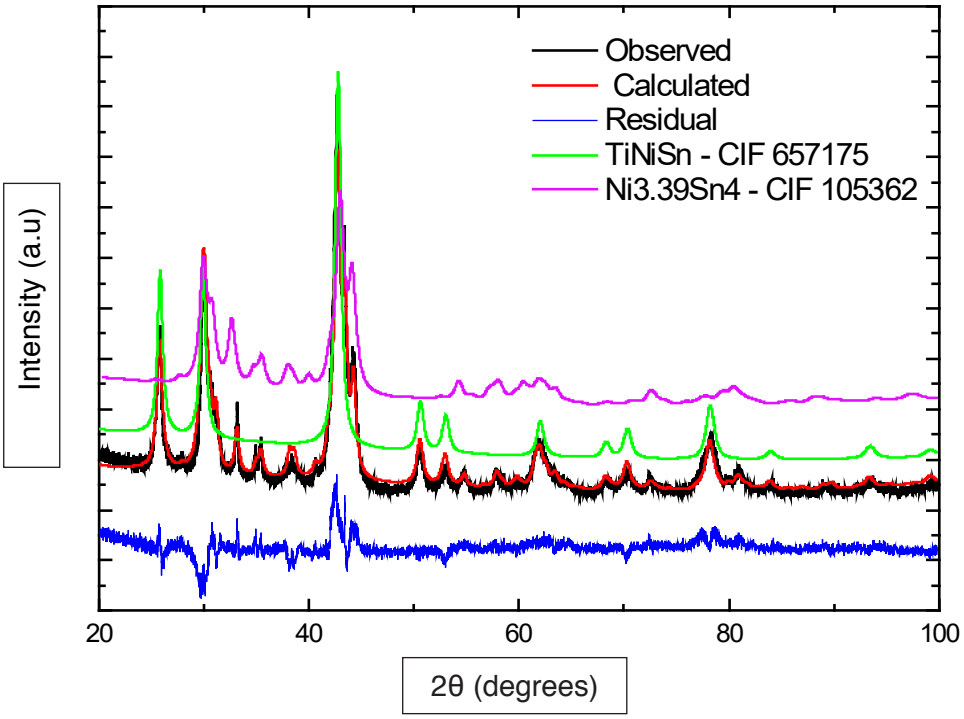
Figure 4: XRD measurement of the sample milled for 4 hours and annealed at 380˚C

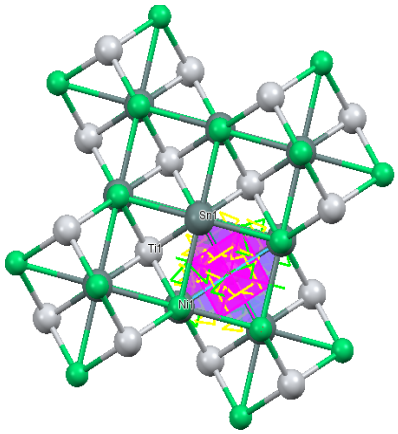


Source: Created by the author

With the Rietveld method, data such as unit cell volume, atomic density, crystalline lattice shape and parameter were obtained, however this information is not sufficient to determine properties as the lattice's thermal and electric conductivity.

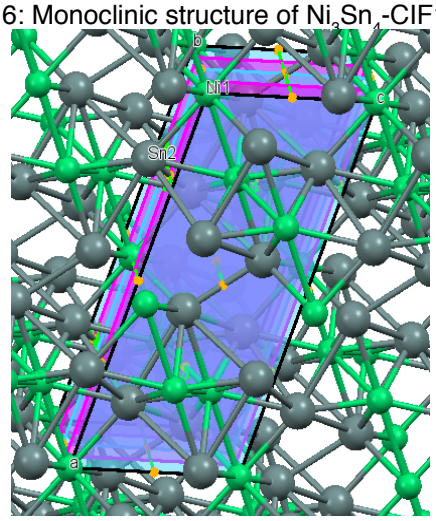
The two major thermal events observed on the DSC measurement at the temperatures at 260˚ C and 400˚C were found out to be the crystallization of two distinct phases, that are Ni_3Sn_4 and $Ni_{3.39}Sn_4$, respectively. The phases were determined through the Rietveld method, which calculated the lattice profiles and matched with the XRD measurements of the processed powder.

Figure 5: Cubic structure of TiNiSn-CIF 657175



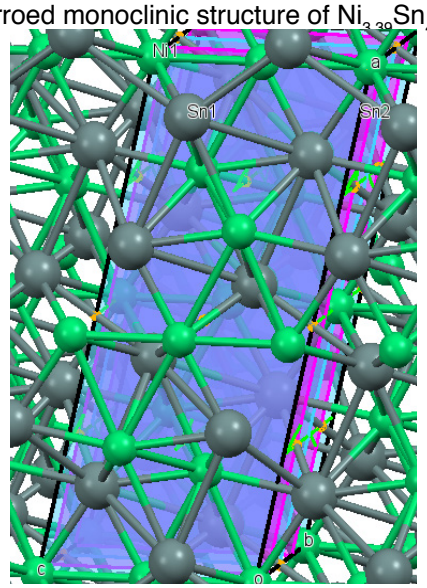
Source: The Cambridge Crystallographic Data Centre

Figure 6: Monoclinic structure of Ni_3Sn_4-CIF105363



Source: The Cambridge Crystallographic Data Centre

Figure 7: Mirroed monoclinic structure of $Ni_{3.39}Sn_4$-CIF105362



Source: The Cambridge Crystallographic Data Centre

Information such as mean crystallite size and structural microdeformation can be obtained through algebraic calculation, using functions provided by the GSAS program manual [4]. The defined variable that represents the crystallite size is ***p***, while ***s*** represents microdeformation and **RwP** represents the qualitative parameters of the refinement. For each present phase, in each sample, the crystallite size and microdeformation values were calculated using equations 1 and 2.

$$p = \frac{18000K_s\lambda}{\pi LX} \quad \text{eq. 1}$$

$$s = \left(\frac{\pi}{18000}\sqrt{8ln2(GU - GU_0}\right) \quad \text{eq. 2}$$

The parameters in question are shown below.

Table 3: Calculated structural parameters

Sample	Phase	Microdeformation (%)	Crystallite Size (nm)
TiNiSn 4H	TiNiSn – CIF 657175	0.02	18.8
TiNiSn 4H	NiTi – CIF 646967	0.03	13.6
TiNiSn 4H @ 310° C	TiNiSn – CIF 657175	3.99	25.2
TiNiSn 4H @ 310° C	NiTi – CIF 646967	1	13.98
TiNiSn 4H @ 310° C	Ni_3Sn4 – CIF 105363	2.17	20.5
TiNiSn 4H @ 380° C	TiNiSn – CIF 657175	2.80	36.7
TiNiSn 4H @ 380° C	$Ni_{3.39}Sn_4$ – CIF 105362	1.63	14.9

Source: Created by the author

Table 4: Rietveld method qualitative parameter obtained through GSAS calculations

Sample	wRp
TiNiSn 4H	0.0926
TiNiSn 4H TT 310° C	0.01136
TiNiSn TT 380° C	0.0903

Source: Created by the author

4 . CONCLUSION

Based on the obtained results through the XRD analysis, as well as the comparison between the profiles between the samples and PDF2003 database, using the software PANalytical X'Pert HighScore Plus, it can be affirmed that the nanostructured alloy TiNiSn can be synthesized through Mechanical Alloying (in stoichiometric proportions of 1:1:1), dispensing the need for additional synthesis methods such as Spark Plasma Sintering[5] e Mechanically Activated Annealing[10].

The obtained results from the refinement through the Rietveld method indicates that the samples milled for 3 and 4 hours show biphasic cubic crystalline structure; in the sample milled for 3 hours, the obtained material had the profiles of the alloys Full Heusler (Ni_2TiSn) and Half Heusler (TiNiSn), while that in the sample milled for 4 hours it is also verified the existence of the Half Heusler alloy; a NiTi phase is also present in the material.

In addition to these data, the Rietveld method proved to be efficient on providing information about the material's structure, as well as the crystallite size and phase microdeformation. Further analysis of the DSC measurement indicates that two exothermic events happened at approximately 260° C and 400° C. The XRD measurements alongside the Rietveld method refinements of the annealed samples reveal that the exothermic events observed on the DSC thermogram are correspond to the crystallization of two phases Ni_3Sn_4 and $Ni_{3.39}Sn_4$, respectively.

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