Quantitative phase analysis from powder diffraction using de Rietveld method in hydrogen storage alloys based on TiCr

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Abstract. Hydrogen storage is one of the important steps in the implementation of the hydrogen economy; metal hydrides are a promising way to achieve this goal. We present in this work the use of Rietveld analysis to characterize structurally TiCr-based alloys that are able to store hydrogen. TiCr1.1V0.9, TiCr1.1V0.45Nb0.45, TiCr1.1V0.2 Nb0.8, TiCr1.1Nb0.9 alloys were synthesized in an arc furnace under argon atmosphere. The analysis of phases was developed by X-Ray Diffraction (XRD) for further refinement of both the two lattice parameters and the percentage of the phases. Our results confirmed that a structure bcc, mostly combined with a small percentage of Laves phases, leads to obtain important properties in this area.

1. Introduction
Hydrogen storage is one of the keys to implement a new global energy vision based on this gas, the methods currently used are pressurized tanks, cryogenic tanks and metal hydrides [1]. The last one has advantages for its large storage capacity and safety, and for these are used alloys with transition metals such as Mg which stores 7% by weight of H2 and metals such as Ti, Cr, V, Zr, Nb [2]. Hence the great interest in studying the crystal structure and physic-chemical properties to improve performance in the hydrogen absorption capacity. The X-ray diffraction is one of the most important techniques for characterization of crystalline materials. This has traditionally been used for qualitative analysis, quantitative phase and for the determination of the crystal structure. In recent years their applications have extended to the determination of imperfections in the structure and residual stress measurements. The Rietveld method is a refinement technique that has the ability to determine with accurately structural parameters a crystalline sample, from the construction of a theoretical model that fits at the experimental diffraction pattern by the least squares method. In the theoretical model are included structural aspects such as crystal structure, space group, position of atoms in the unitary cell, etc. Also, in the theoretical model are included microstructural factors that consider the concentration of the phases present, crystal size and microstrains. The instrumental factor is also included, which contemplates the effect of optical diffraction equipment X-ray on the measurement and whose effect is the broadening of the diffraction peaks [3].

In this paper is studied the effect on the lattice parameters and on the quantification of the phases by replacing V by Nb in based alloys on TiCrV used for hydrogen storage, by the Rietveld method by using the fullprof program.
2. Experiment methodology
Button shaped ingots of TiCr$_{1.1}$V$_{0.9}$, TiCr$_{1.1}$V$_{0.45}$Nb$_{0.45}$, TiCr$_{1.1}$V$_{0.2}$Nb$_{0.8}$, TiCr$_{1.1}$Nb$_{0.9}$ alloys with weights of 20g were prepared by arc melting in argon atmosphere, using high-purity materials (>99.95). The samples were melted 3 times in order to achieve a homogenized microstructure.

For structural study was necessary to use the sample metal powder which passed through a mesh of 270 microns, following which it was subjected to XRD using a Shimadzu 5000 with Cu-K$\alpha$ radiation, the lattice parameters and phase present in the samples were calculated by the Rietveld method using the software Fullprof.

3. Analysis and discussion of results
Figure 1 shows X-ray diffraction patterns for the alloys. Figure 1(a) shows a typical bcc structure type (Im3m space group) for the TiCr$_{1.1}$V$_{0.9}$ alloy [4]. As is known in the TiCr binary phase diagram, the stoichiometric ratio TiCr$_{1.1}$ crystallizes in Laves phase [5].

When an element like Vanadium (V) is mixed, the inhibition of the formation of Laves phase in the melting process is presented [6], producing a bcc structure, as is observed in figure 1.a. It is also noted that the V inhibits the increase of Laves phase when Niobium (Nb) is added. However, when the Nb content is increased and the V content decreased, the amount of Laves phase C14 increases, coexisting with the bcc structure as it is shown in Figures 1(b) and 1(c). When V is completely replaced by the Nb, the Laves phases raised significantly.

The Laves phases are presented in compounds or alloys where the ideal ratio of atomic sizes between neighboring atoms A and B is $\sqrt{(3/2)}$=1.225; however, experimentally they are in a range of solubility between 1.06 and 1.67. This feature is presented by the geometric factor of atoms due to the property of contract and expand so that approximates the ideal ratio [7]. Therefore, the geometric rule is important for predicting behaviors of Laves phases.

In this work is expected that the TiCr$_{1.1}$Nb$_{0.9}$ alloy crystallizes a Laves phase, since each pair of elements fit the ideal reason $\approx$1.225 ($R_{Nb}/R_{Cr}$=1.15 and $R_{V}/R_{Cr}$=1.14). Thus, the ternary alloy TiCrNb...
meets the geometric principles for the formation of Laves phases coexisting with a bcc structure, as observed in the diffractogram Figure 1(d). This is expected in the transition metals due to the relative similitude of the atomic radii of the metal elements (R_{Nb}=1.468\text{Å}, R_{Ti}=1.462\text{Å}, R_{Cr}=1.282\text{Å}).

It is observed an increase in lattice parameters for a bcc structure, with high intensive to lower angles. The lattice parameters and the percentage of the phases present are calculated by the Rietveld method using the fullprof program, and are the results are presented in Table 1. The graphics of Rietveld analysis are shown in Figure 2.

Table 1. Rietveld analysis results for the calculate the lattice parameters and the percentage of the phases present in the different alloys.

| Sample                  | S   | $R_{wp}$ | Phase | % Phase | Lattice Parameters (Å) |
|-------------------------|-----|----------|-------|---------|------------------------|
| TiCr$_{1.1}$V$_{0.9}$   | 1.40| 12.36    | bcc   | 100.00  | a=3.06                 |
| TiCr$_{1.1}$V$_{0.45}$Nb$_{0.45}$ | 1.78| 28.08    | bcc   | 99.50   | a=3.10                 |
| TiCr$_{1.1}$V$_{0.2}$Nb$_{0.8}$ | 1.75| 22.40    | C14   | 0.50    | a=4.94, b=8.15         |
| TiCr$_{1.1}$Nb$_{0.9}$  | 5.87| 27.20    | bcc   | 97.50   | a=3.15                 |
| TiCr$_{1.1}$V$_{0.2}$   | 5.87| 27.20    | C14   | 2.50    | a=5.18, b=9.56         |
| TiCr$_{1.1}$Nb$_{0.9}$  | 5.87| 27.20    | C14   | 15.00   | a=4.90, b=8.14         |
Figure 2. Rietveld Analysis of the samples (a) TiCr$_{1.1}$V$_{0.9}$, (b) TiCr$_{1.1}$V$_{0.45}$Nb$_{0.45}$, (c) TiCr$_{1.1}$V$_{0.2}$Nb$_{0.8}$, (d) TiCr$_{1.1}$Nb$_{0.9}$.

The *Rietveld* method is based on the relationship:

$$S_y = \sum W_i (y_{i\text{obs}} - y_{i\text{cal}})^2$$  \hspace{0.2cm} (1)

In this function the $y_{i\text{obs}}$ and $y_{i\text{cal}}$ are the experimental and calculated intensity at point $i$ of the diffraction pattern respectively, $W_i$ is the respective weight given to these intensities while the summation is over all points of the pattern diffraction. One way of following the progress of the refinements is naturally to watch the decrease of this least-squares residual. In most cases the residual value is normalized and expressed as:

$$R_{pw} = \left( \frac{w_i \sum (y_{i\text{obs}} - y_{i\text{cal}})^2}{\sum w_i (y_{i\text{obs}})^2} \right)^{1/2}$$ \hspace{0.2cm} (2)

The values shown in Table 1 have a good approximation of the quantification of the phase present in each alloy and the calculation of the lattice parameters. The discontinuity in Figure 2 of the *Rietveld* analysis does not affect the measure because of the convergence of the algorithm.

Since the number of atoms and atomic radii of Ti (1.462Å) and Nb (1.468Å) are larger than atoms and atomic radii of Cr (1.282Å) and V (1.34Å), the lattice parameter increases for the different samples. This leads to an increase in the lattice parameter, as far that vanadium is substituted for niobium.

The fact that the unit cell of the bcc structure is increased is supported by the empirical *law of Vegard*, which describes the increase or decrease linear lattice parameter as a function of the concentration of the constituent elements of the alloy. Yoo *et al.* [8] reported this phenomenon, where they observed a reduction of network parameters when they were added by small percentages of Cr in the Fe alloy Ti$_{0.32}$Cr$_{0.43}$V$_{0.25}$.

4. Conclusions

Substituting V by Nb in the alloy TiCr$_{1.1}$V$_{0.9}$ was studied. In this work we verified that the compounds TiCr$_{1.1}$V$_{0.45}$Nb$_{0.45}$, TiCr$_{1.1}$V$_{0.2}$Nb$_{0.8}$ and TiCr$_{1.1}$Nb$_{0.9}$ give rise to a double-phase structure made up of primarily a bcc structure and a smaller Laves C14 cubic-type structure.

Substituting the V by Nb the lattice parameters increases this is a good indicator for the type of alloys from hydrogen storage.

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