Structural study of hydrogen absorption properties using Thermocalc software for application in energy storage

D Bellon¹, A Martínez-Amariz¹,², and E Montes³

¹ Grupo de Investigación Nuevas Tecnologías, Universidad de Santander, Bucaramanga, Colombia
² Materials Science and Technology Research Group, Foundation of Researchers in Science and Technology of Materials, Colombia
³ Grupo de Investigación en Ciencias Básicas Aplicadas, Unidades Tecnológicas de Santander, Bucaramanga, Colombia

E-mail: dan.bellon@mail.udes.edu.co

Abstract. The interest in developing experiments and processes in general through mathematical modelling or simulation, has been growing considerably in recent decades; the previous, insofar as it offers highly reliable results that have an impact on advantages such as reduction of the risk associated with the execution of costly or difficult to reproduce experiments since they handle many variables or even the elimination of times associated with the execution of said experiments. For its part, the study of hydrogen storage alloys represents a fundamental element in the so-called hydrogen economy, which seeks the integration of hydrogen as an alternative solution to dependence on fossil fuels, due that this energy vector has a high energy density when is compared to the gasoline and the only residue of this process is water vapor that will undoubtedly reduce CO₂ emissions. Thus, in this study a simulation of the evolution of the microstructure of hydrogen storage alloys based on TiCrV is developed, using ternary systems at different temperatures; this evolution is the result of the phase change when the elements are subjected from high temperatures to room temperature, obtaining a body-centered cubic structure. Likewise, the solidification process of the components present in the alloy is studied to corroborate the final structure with experimental data. In preliminary results, it is observed that the simulation throws a body centered structure, and in the solidification process, a remnant of a compact hexagonal structure is observed. This Ti-Cr-V system is widely studied due to its large hydrogen storage capacity, which can be used for technological purposes.

1. Introduction

The hydrogen economy is a concept that has become increasingly relevant in the energy field, due it offers various favorable environmental conditions such as clean, efficient and renewable energy. However, for hydrogen to compete in the energy market, a safe and efficient storage system is necessary. Several forms of hydrogen storage have been widely studied [1], including metal hydrides, which are increasingly attractive to different research centers worldwide, since they have interesting characteristics such as high volumetric capacity and operating pressures relatively low [2].

TiCrV base alloys have been extensively studied [3-6] and are promising for the improvement the hydrogen absorption kinetics thanks to their body-centered cubic structure (bcc) structure that yields a better hydrogen diffusion coefficient, at room temperature and at moderate pressures [7-8].
maximum storage capacity at room temperature is 3.7% [9]; however, the desorption capacity is much lower, and although they have a higher absorption capacity, they usually have a long incubation time during the first hydrogenation [9-10]. The ternary system is a mixture of three elements in different compositions, which can form different compounds at different temperatures. This system can be of great application in energy storage to supply current storage systems with high efficiency. The study of this type of systems has advantages at the environmental level, by generating as the only residue water vapor.

On the other hand, the theoretical simulations associated with the storage of hydrogen in the solid state by means of metal hydrides have helped to understand the experimental results, as well as the prediction and design of stoichiometric relationships with better properties [11], which leads to the optimization of times and resources of the investigation. Thermocalc is a software with a wide database, based mainly on the calculation of phase diagrams, for the generation of all types of phase equilibria, phase diagrams, phase transformation calculations, and thermodynamic evaluations; Thermocalc is a software of thermodynamic calculations to address mineral balance problems [12-13].

In the present work, a TiCrV base alloy was theoretically studied, with the following stoichiometric ratio TiCr\textsubscript{1.1}V\textsubscript{0.9} by using the Thermocalc software. The simulation results allowed to characterize the phases formed during the solidification of the TiCrV system. These simulated ternary diagrams are constructed for slow cooling conditions and pressures close to atmospheric pressure; therefore, they are valid under conditions of thermodynamic equilibrium. Finally, the results of the simulation were corroborated with the structure found experimentally.

2. Experimental procedure
Computational simulations were carried out using the Thermocalc software, to obtain the ternary phase diagrams and the respective cooling curve. For the experimental process, Ti was used with a purity of 99.70%, Cr with a purity of 99.99% and V with a purity of 99.70%. The alloys were produced by arc fusion; the electric arc furnace used in the foundry process was the Bühler brand located at the Federal University of Rio de Janeiro. The samples having a high susceptibility to oxidation were fused under argon gas, which is an inert gas of high purity. The fusion of the mixture was carried out directly by an arc in a copper crucible of high purity. The stoichiometry of the alloy and the calculation of the different percentages were made based on a load of 30 grams and are presented in Table 1. The alloy was melted and remelted 3 times to ensure its homogenization.

| Element | Mass (gr) | %wt. |
|---------|-----------|------|
| Ti      | 9.52      | 31.73|
| Cr      | 11.36     | 37.89|
| V       | 9.11      | 30.38|
| Total   | 30.00     | 100.00|

Regarding characterization, it was carried out by X-ray diffraction (XRD), which allowed to identify the different crystalline phases present. In this experimental test, the radiation used was Cu-K\textalpha, the wavelength was 1.54 Å. The normal working conditions were: voltage = 40 kV, current = 30 mA, sweep speed in 2θ = 0.02 degrees for 4 seconds. And the analysis track was from 20° to 80°. The analysis time for each sample was 100 minutes. The results of the computational simulation for obtaining the TiCrV ternary phase diagram and the respective slow cooling curve from 2000 °C up to room temperature (25 °C) and at atmospheric pressure, were contrasted with the results of the experimentally obtained XRD.

3. Results and discussion
The results of the thermodynamic simulation using the Thermocalc program allowed us to characterize the phases formed during the solidification of the TiCrV ternary system. The simulated ternary
diagrams were constructed for slow cooling conditions and pressures close to atmospheric pressure. Therefore, the diagrams are valid under conditions of thermodynamic equilibrium (see Figure 1 to Figure 6).

Figure 1. Isothermal cut of the ternary phase diagram Ti-Cr-V at 2000 °C.

Figure 2. Isothermal cut of the ternary phase diagram Ti-Cr-V at 1500 °C.

Figure 3. Isothermal cut of the ternary phase diagram Ti-Cr-V at 1000 °C.

Figure 4. Isothermal cut of the ternary phase diagram Ti-Cr-V at 800 °C.

Figure 5. Isothermal cut of the ternary phase diagram Ti-Cr-V at 500 °C.

Figure 6. Isothermal cut of the ternary phase diagram Ti-Cr-V at 25 °C.
In the Figure 1 to Figure 6, the different isothermal cuts of the ternary diagram of the TiCrV system obtained through the simulation by Thermocalc are shown, at temperatures of 2000 °C, 1500 °C, 1000 °C, 800 °C, 500 °C and 25 °C respectively; there it can be seen that the solidification of the alloy occurs between 2000 °C and 1500 °C, with the formation of the crystalline phase bcc1. Around 800°C, two bcc phases coexist. The bcc1 phase is stable at high temperatures, contrary to the bcc2 phase, which is only stable in a temperature range between 1000 °C and 500 °C. On the other hand, the bcc2 phase is transformed to HCP between 800 °C and 500 °C. The HCP phase is formed due to the titanium content in the studied alloy and is stable at low temperatures.

Figure 7 shows the cooling curve of TiCr1.1V0.9 alloy calculated by Thermocalc. The simulation of the slow cooling of this alloy was carried out at a pressure of 1.013 Pa (1.013 Pa = 1 atm). It can be observed that solidification occurs at 1560 °C, where the present matrix has a bcc1 structure. This structure is maintained until 868 °C, the temperature at which the formation of another bcc2 structure coexisting with the bcc1 structure occurs. The bcc2 phase is stable only in a temperature range between 868 °C and 662 °C. Below 664 °C it is transformed into HCP structure, which coexists with the bcc1 phase up to room temperature. The phase fraction bcc1 and HCP present in the alloy matrix at room temperature are 82% and 18%, respectively.

Figure 8 shows the XRD pattern of the TiCr1.1V0.9 alloy sample; the diffractogram exhibits a body-centered cubic crystalline structure, except for a minimum amount corresponding to the diffraction with position 2θ° = 40°. The BCC phase is characteristic of TiCrV alloys as reported in the literature [14]. The addition of vanadium to the TiCr alloy inhibits the formation of the Laves phases during the solidification process [15-17] and, therefore, the TiCrV alloys present a single bcc phase, as was found in the simulation by Thermocalc. The network parameter of the bcc phase corresponding to the alloy of TiCr1.1V0.9 obtained by manual crushing was 3.0586 Å.
The diffraction other than the bcc phase, found in position \(2\theta = 40^\circ\) is described by Huang Taizhong, which corresponds to the phase \(\text{Ti}_{1.07}\text{Cr}_{1.93}\) which does not fully solubilize in the bcc phase of the alloy [18].

### 4. Conclusions

The simulation developed through the Thermocalc software allowed us to analyze the \(\text{TiCr}_{1.1}\text{V}_{0.9}\) alloy, clearly identified a bcc structure. This has been corroborated by the analysis of XRD. This is value due to the simulation is increasingly important in the investigative and experimental processes since it allows to mitigate times and costs. Likewise, the ternary diagrams are not trivial, and the software allows to study and make a better analysis of the interactions between the metals.

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