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Hydrogen determinations in a zirconium based alloy with a DSC

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Abstract

In the present work a method to measure hydrogen concentrations in zirconium-based alloys was developed measuring simultaneously both, the temperature of terminal solid solubility, T_{TSSd}, and the hydride dissolution heat, $Q_{\delta\to\alpha}$, using a differential scanning calorimeter (DSC). The hydrogen concentration measured with that technique, $[\mathrm{H}]_{\mathrm{Q}}$, and the values obtained with a standard hydrogen gas meter, $[\mathrm{H}]_{\mathrm{HGM},}$ shows a linear relation: $[\mathrm{H}]_{\mathrm{Q}} = (1.00 \pm 0.03)[\mathrm{H}]_{\mathrm{HGM}|} + (9.2 \pm 8.0)$ with a correlation factor of 0.99 in the entire solubility interval in the αZr phase, from 15 to 650 wt. ppm-H. The mean enthalpy value determined with two different criteria for T_{TSSd} and $Q_{\delta\to\alpha}$ measurements is $\Delta H^{(\mathrm{Q})}_{\delta\to\alpha} = 39.3 \pm 1.5$ kJ/mol H. The present method is specially appropriate for alloys where a partition of the overall hydrogen concentration in two phases exists. It is applicable to all hydride forming metals which ideally follows the van't Hoff law.

Keywords: DSC; Hydrogen solubility; Enthalpy; Zircaloy-4

1. Introduction

During the last decade differential scanning calorimetry has been applied to the study of the solvus in the Zr–H system. By means of this technique the temperatures of terminal solid solubility in dissolution, T_{TSSd}, and precipitation, T_{TSSp}, have been determined in zirconium-based alloys used in the nuclear industry [1–5]. The solvus line is built with T_{TSSd} values taken from the calorimetric curve of hydride samples of known hydrogen concentrations.

In a recent work [6,7] the DSC technique was successfully applied to the accurate determination of the zirconium hydride dissolution enthalpy in the αZr matrix, $\Delta H_{\delta\to\alpha}$, by measuring the $Q_{\delta\to\alpha}$ and the T_{TSSd} values in Zircaloy-4 specimens of different hydrogen concentrations.

As $Q_{\delta\to\alpha}$ is proportional to the number of moles of hydrides dissolved, if $\Delta H_{\delta\to\alpha}$ is known and constant [8,9] along the solubility range, the measurement of $Q_{\delta\to\alpha}$ allows to obtain the number of moles of the hydride phase dissolved, $n_{\delta,}$ by the equation:

$$Q_{\delta\to\alpha} = \Delta H_{\delta\to\alpha} n_{\delta}. \qquad (1)$$

The present method is being applied to the study of neutron irradiated Zircaloy-4, where a partition of the bulk hydrogen concentration occurs remaining a fraction of the hydrogen concentration trapped in defects created by radiation instead of precipitating as hydrides [10,11]. It also can be applied to measure hydrogen amounts precipitated as hydrides in samples taken from pressure tubes of CANDU type reactors. In this structural components manufactured with the two-phase alloy Zr2.5%Nb a similar partition between the hydride forming αZr phase and βZr phase stabilized by niobium occurs [3].

The present work is organized in the following way: Section 2 describes the calorimetric curve of a hydride dissolution process, the criteria used to measure T_{TSSd} and $Q_{\delta\to\alpha}$, the thermodynamics of the terminal solubility, the material scheduling and the DSC experimental conditions. Section 3 presents the results and discussion. Finally the conclusions are presented in Section 4.

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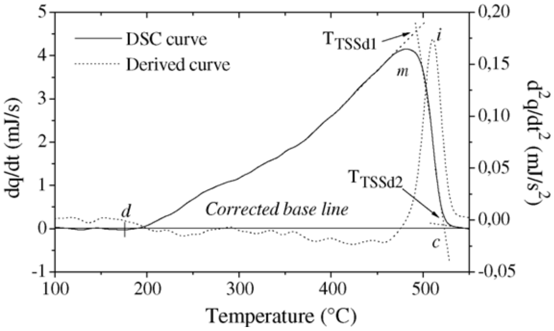

Fig. 1. Heating curve of a hydrided Zircaloy-4 sample (480 ppm-H).

2. Experimental

2.1. Calorimetry

In calorimetry the curve, dq/dt (mW) versus T (°C), obtained in a calorimetric run with empty crucibles is called *base line*. The base line for a DSC is usually a horizontal straight line.

For a Zircaloy-4 sample containing hydride precipitates, a curve like the one shown in Fig. 1 is obtained. The curve deviates from the straight base line in the interval 150–170 °C (point d, temperature T_d), indicating the start of the dissolution process. That interval corresponds to a solid solubility of 4–6 ppm of hydrogen. When the transformation is completed the original base line is recovered. The slope change determines a maximum value at the point m (temperature T_m) and the return to the original base line defines a completion point c (temperature T_c).

2.2. T_{TSSd} and $Q_{\delta\to\alpha}$ determinations

The T_{TSSd} value in the calorimetric curve is between T_m and T_c temperatures. Based on the referenced Kearns curve, some authors choose T_m as the T_{TSSd} [2–4,12]. Others, based on accuracy criterion arguments [1], choose a temperature associated to the inflection point observed in the calorimetric curve between the points m and c (point i, temperature T_i). However, the recovery of the base line occurs at the completion point, c, where the dissolution effects on the calorimetric curve vanish [6]. Since the uncertainty interval of the technique is given by the $T_c - T_m$ interval, these two temperatures were measured in the present work. As occasionally the calorimetric curve is rather shallow and/or waved around the point m, the corresponding temperature T_m was measured at the intersection point of the linear extrapolation from both sides of the curve, from now on T_{TSSd1}. The same criteria were taken for defining T_c, from now on T_{TSSd2}.

In the calorimetric run of a hydrided sample the heat of dissolution, $Q_{\delta\to\alpha}$, is the area limited by the calorimetric curve and the base line between points d and c of the Fig. 1, and it is obtained through numeric integration [6].

2.3. Solvus thermodynamics

van't Hoff's equation results from the equilibrium condition between two phases: the αZr phase, in which a fraction of the hydrogen content is in solid solution and the δ-hydride phase [13]. Posing equality between their chemical potentials results in:

$$\ln X = \frac{\Delta S_{\delta\to\alpha}}{R} + \frac{\Delta H_{\delta\to\alpha}}{RT} \tag{2}$$

where X is the hydrogen atomic fraction (H/Zr), R the ideal gas constant, $\Delta S_{\delta\to\alpha}$ the dissolution entropy and $\Delta H_{\delta\to\alpha}$ the enthalpy. If Eq. (2) is combined with Eq. (1), we obtain:

$$\ln X_{\text{normal}} = \frac{\Delta S_{\delta\to\alpha}}{R} + \frac{\Delta H_{\delta\to\alpha}}{RT} \tag{3}$$

being

$$X_{\text{normal}}^{(Q_i)} = \frac{Q_{\delta\to\alpha}}{n_{\text{Zr}}\Delta H_{\delta\to\alpha}^{(\text{ref})}} \tag{4}$$

where n_{Zr} are the Zr moles of the sample and $\Delta H_{\delta\to\alpha}^{(\text{ref})}$ is a normalization factor for $Q_{\delta\to\alpha}$, the dissolution enthalpy of the δ-hydride phase in αZr, 37.7 kJ/mol H [6].

From Eq. (3), by measuring $Q_{\delta\to\alpha}$ and T_{TSSd}, $\Delta H_{\delta\to\alpha}$ may be obtained without knowing the hydrogen concentration of the sample, which is normally obtained using a hydrogen gas meter. With this $\Delta H_{\delta\to\alpha}$ value and the $Q_{\delta\to\alpha}$ value corresponding to the Zircaloy-4 sample, the quantity of hydrogen is determined through Eq. (5).

$$n_{\text{H}} = \frac{Q_{\delta\to\alpha}}{\Delta H_{\delta\to\alpha}} \tag{5}$$

2.4. Materials

The material is taken from a cold rolled sheet of Zircaloy-4. Its chemical composition is shown in Table 1. Pieces 10 cm × 1 cm with a 1.8 mm thickness were cut from this material and subjected to a 2.5 h recrystallization treatment at

Table 1
Chemical composition of the Zircaloy-4 sheet

Alloying elements (wt.%)	
Sn	1.49
Fe	0.20
Cr	0.11
Impurities (ppm wt.%)	
O	0.14
Ni	49
Hf	99
Al	39
Co	18
Cu	30
Mn	36
Mo	8
Ti	3
U	1.5
W	25

750 °C. The resulting microstructure consists of a 15–20 μm diameter equiaxed grain.

2.4.1. *Hydriding*

The material was cut into 5 cm × 1 cm pieces that were mechanically polished and scaled with a distilled water, HNO_3 and HF solution. They were afterwards subjected to an ion sputtering with argon followed by a palladium coating. The hydrogen was added by performing thermal treatments at 400 °C in a hydrogen atmosphere (99.999%) at 2.5 kg/mm^2 pressure for 1/4 to 3 h periods. In this way, concentrations covering practically the entire solubility range in αZr phase were achieved.

After hydriding the samples received a 3-h thermal treatment at 450 °C in order to incorporate the hydride layer formed on the surface into the bulk, homogenizing in this way the hydride distribution. This was performed under a N_2 atmosphere.

Both in the hydriding and homogenization treatments, the samples were slowly left to cool inside the furnace. This type of cooling favors the formation of the δ equilibrium phase. Some of the hydrided material pieces were analyzed with X-ray diffraction to identify the hydride phases present in the samples. As expected, where the hydride presence could be detected (the technique's detection limit is around 70 ppm), the δ equilibrium phase with $ZrH_{1.5}$ and $ZrH_{1.66}$ stoichiometric relations was observed. Phase ε or the metastable γ [14] were found in a very few cases.

For DSC experiments, 24 samples of 4 mm × 4 mm × 1.5 mm and masses between 150 and 155 mg were cut. Their concentrations were between 15 and 650 ppm.

Previous to the runs in the DSC, a 1/2 h solubilization treatment was given to each sample at 550 °C (eutectoid temperature) to ensure a homogeneous hydride distribution.

2.5. *Experiments in DSC*

The calorimeter used is a heat flux type, (model DSC-60 by Shimadzu, Japan) which has been already described [10]. The temperature axis has been calibrated using the fixed points of indium and zinc while the enthalpy changes with the latent heat of fusion of these two metals. Their fixed points are 156.6 °C (indium) and 419.6 °C (zinc), which are convenient for the hydrogen solubility range in αZr phase. The latent heats of fusion are 28.45 and 100.50 J/g, respectively. The experiments were made under a dynamic N_2 (99.998%) atmosphere of 25 ml/min. The program of experiments considered a series of three to four runs per sample at a heating rate of 20 °C/min, because as was shown in previous works [6,7] it is the most reliable heating rate to assure a good balance between the DSC sensitivity and the thermal homogeneity of the sample. Cooling was made at the same rate.

The maximum programmed temperature (T_{max}) in each run was 550 °C. The repetition of runs under identical experimental conditions allowed us to assure the technique's reproducibility, calculating averages for T_{TSSd}, $Q_{\delta\rightarrow\alpha}$ and the measurements' statistical errors and dispersions.

The T_{TSSd} error is around 1.5 °C. Regarding $Q_{\delta\rightarrow\alpha}$ measurements, the estimate is around 6% for hydrogen concentrations higher than 100 ppm.

Once the whole series were done, the hydrogen concentration of each sample was measured with a hydrogen gas meter (HGM) LECO RH-404 by the technique of fusion extraction under inert gas atmosphere. The error of these measurements is about 4 ppm.

3. Results and discussion

3.1. *Transformation heats and temperatures*

Since the DSC has never been used to measure $Q_{\delta\rightarrow\alpha}$ in the direct way pointed out in Section 2.2, the discussion in the literature regarding the point associated to the T_{TSSd} position in the calorimetric curve do not exist concerning $Q_{\delta\rightarrow\alpha}$ determinations. The usual criterion for transformation heat measurement consists in calculating the area limited by the base line interpolation between points d and c and the calorimetric curve (Fig. 1). Although this is a very general criterion [15], phenomena such as the melting of a pure substance, an amorphous crystallization or a chemical reaction occur within a very close temperature range, which is thus different from that of the hydride phase dissolution in a Zr alloy. In this case, the difference among the temperatures established in point m of the DSC curve, T_{TSSd1}, and c, T_{TSSd2}, in Fig. 1, is between 25 and 30 °C, while the one observed in the curve corresponding to the melting point of an indium standard used for the DSC calibration is ~4 °C. This has led us to broaden the criterion to determine $Q_{\delta\rightarrow\alpha}$ applying the same criteria as the one established for T_{TSSd}. We have considered measuring the area between points d and c in Fig. 1 following the usual criterion for this technique, and also between points d and m, being these values respectively called Q_2 and Q_1. Table 2 shows the results obtained in the measurement of T_{TSSd1}, T_{TSSd2}, Q_1 and Q_2. In addition, the hydrogen determinations carried out with the HGM and the masses of each sample are shown in Table 2 too.

3.2. *van't Hoff plots and [H] calculations*

By making the modified van't Hoff's graphs (Eq. (3)), we obtain:

$$\ln X_{\text{normal}}^{(Q_1)} = 3.16 - \frac{4789}{T_{TSSd1}}; \qquad (6)$$

$$\ln X_{\text{normal}}^{(Q_2)} = 2.88 - \frac{4662}{T_{TSSd2}}. \qquad (7)$$

The high linearity observed ($R = -0.99$) shows the ideality of the Zr–H system in agreement with van't Hoff's equation. Fig. 2 shows the linear regressions and experimental data. The slope is the $\delta ZrH_{1.5} \rightarrow \alpha Zr$ transformation enthalpy.

Table 2
Hydrogen contents measured with the hydrogen gas meter (HGM), sample masses, $Q_{\delta\to\alpha}$ values and $T_{\mathrm{TSSd1;2}}$ values

$[\mathrm{H}]_{\mathrm{HGM}}$ (ppm)	Weight (mg)	Q_1 (mJ)	Q_2 (mJ)	T_{TSSd1} (°C)	T_{TSSd2} (°C)
15	155.16	40	63	193.0	213.6
15	155.04	25	44	194.6	216.7
79	155.20	211	255	299.4	323.5
83	155.19	279	326	303.5	320.6
87	155.20	262	315	309.6	328.0
108	155.15	329	415	310.8	349.5
104	155.01	320	369	324.4	345.7
110	155.14	318	362	329.2	352.8
186	155.20	763	855	378.3	402.1
189	155.20	610	706	377.3	402.9
190	154.85	693	790	376.4	407.0
198	154.80	685	769	380.1	403.9
198	155.15	757	856	379.8	406.7
242	155.05	993	1123	400.1	426.4
250	155.16	995	1187	402.3	438.3
292	155.13	898	1004	425.7	449.3
397	155.12	1239	1362	458.7	482.3
485	154.93	1567	1756	478.5	505.4
490	155.20	1792	1945	482.9	506.3
527	155.15	1842	1990	494.6	517.2
547	155.01	1749	1913	496.9	520.4
570	155.18	1876	2034	503.4	526.3
620	155.13	2087	2266	512.4	536.7
645	155.20	2537	2715	518.8	540.9

The enthalpy values obtained according to the maximum and completion criteria are then $\Delta H_{\delta\to\alpha}^{(Q_1)} = 39.9 \pm 1$ and $\Delta H_{\delta\to\alpha}^{(Q_2)} = 38.8 \pm 1$ kJ/mol H, respectively.

The total T_{TSSd} error is 1.5 °C. In the case of $Q_{\delta\to\alpha}$ the statistical error at the chosen heating rate is 3%, plus the error usually attributed to the DSCs, which is also 3%, so the total $Q_{\delta\to\alpha}$ error is 6%. As observed from these results, the influence of this error on the enthalpy is small.

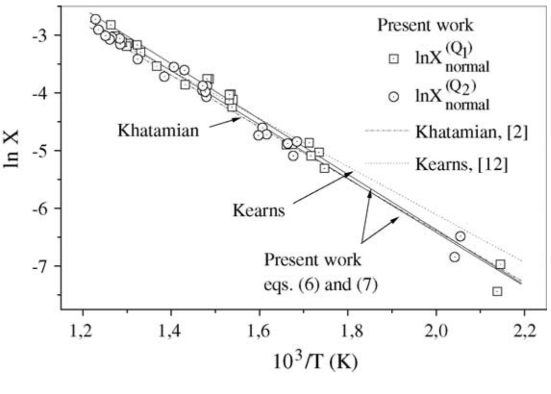

Fig. 2. van't Hoff obtained from $X^{(Q_1)}_{\mathrm{normal}}$, $X^{(Q_2)}_{\mathrm{normal}}$, T_{TSSd1} and T_{TSSd2} values measured in the DSC experiments. Eqs. (6) and (7) are also plotted for a comparison with Kearns and Khatamian results.

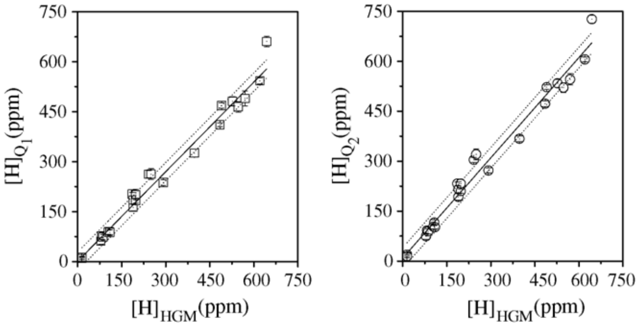

Fig. 3. (a and b) Linear regressions for $[\mathrm{H}]_{Q_i}$ vs. $[\mathrm{H}]_{\mathrm{HGM}}$ between bands given by the standard deviation (28 ppm for $[\mathrm{H}]_{Q_1}$ and 31 for $[\mathrm{H}]_{Q_2}$). The relations are quite linear and the linear regression in 3b is virtually the identity function.

Using the obtained enthalpy values, Q_1 and Q_2 values and the masses of the samples, the hydrogen concentrations corresponding to Q_i ($i = 1, 2$) values, $[\mathrm{H}]_{Q_i}$, were calculated through the following equation:

$$[\mathrm{H}]_{Q_i}(\mathrm{ppm}) = 1600 \frac{Q_i(\mathrm{mJ})}{m_{\mathrm{Zr}}(\mathrm{mgr})\Delta H_{\delta\to\alpha}^{(Q_i)}(\mathrm{kJ/mol\ H})}, \tag{8}$$

but adding to $[\mathrm{H}]_{Q_i}$ the hydrogen that is in solid solution when the dissolution process is detected in the calorimetric run (150–170 °C, point d in Fig. 1). This value is around 5 ppm for Zircaloy-4 according to Kearns solubility curve [12]. Using these values and the hydrogen concentrations measured with the HGM, the $[\mathrm{H}]_{Q_i}$ versus $[\mathrm{H}]_{\mathrm{HGM}}$ graphs observed in Fig. 3a and b were made. The regressions arising from the fitting are

$$[\mathrm{H}]_{Q_1} = (0.90 \pm 0.02)[\mathrm{H}]_{\mathrm{HGM}} + (0.7 \pm 5.5), \tag{9}$$

$$[\mathrm{H}]_{Q_2} = (1.00 \pm 0.03)[\mathrm{H}]_{\mathrm{HGM}} + (9.2 \pm 8.0), \tag{10}$$

being the correlation coefficient 0.99 in both cases. As we can see, the relation is highly linear and both regressions practically turn out to be the identity function, although the $[\mathrm{H}]_{Q_2}$ values are in better agreement with the values obtained with the HGM, also showing the smaller error. In the case of $[\mathrm{H}]_{Q_2}$ error is about 30% for the low concentration region (15 ppm), falls to 11% for 80 ppm concentrations, to 7% for concentration around 100 ppm and under 3% for higher concentrations. In the case of $[\mathrm{H}]_{Q_1}$, the error is about 30% for the low concentration region, falls to 14% for concentrations around 80 ppm, 10% for concentrations around 100 ppm and 4% in average for higher values. The dependency of the experimental error on hydrogen concentration is related to the DSC sensitivity in the $Q_{\delta\to\alpha}$ determination. For low concentrations the signal to be detected in the dissolution is small and the error involved in the base line definition has a higher relative weight on this value [6,7].

As has been shown, the DSC is appropriate to determine hydrogen concentrations in Zr alloys. For concentrations over 100 ppm, the variation in respect of the values obtained with the HGM is relatively low. It has the advantage of not requiring hydrogen standards for its calibration, which do not normally exist for Zr alloys in the market, while the ones used do not have a hydrogen concentration variety (Ti patterns are usually used with 16, 32, 80 and 175 ppm concentrations), since DSCs are calibrated with the latent heat of fusion of pure metals. Moreover, the possibility to repeat the measurements on the same sample allows the limiting of the $Q_{\delta\to\alpha}$ error and consequently the limiting of the $[\mathrm{H}]_{Q_i}$ error.

The main restriction lies in the fact that it can only be used to measure hydrogen concentrations in the αZr phase solubility range. For concentrations of about 650 ppm, the $\alpha\mathrm{Zr}+\delta\to\alpha\mathrm{Zr}+\beta\mathrm{Zr}$ (at 550 °C) transformation occurs, superposing an acute peak to the dissolution curve in Fig. 1, which makes it difficult to measure $Q_{\delta\to\alpha}$. Nevertheless the concentration range of interest for applications in Zr alloy technology is the αZr phase solubility range.

4. Conclusions

The accurate results obtained in hydrogen determination by measuring dissolution heat and enthalpy of hydrides in Zircaloy-4 with a DSC, $\Delta H^{(Q_1)}_{\delta\to\alpha} = 39.9 \pm 1$ and $\Delta H^{(Q_2)}_{\delta\to\alpha} = 38.8 \pm 1$ kJ/mol H, allow us to assert that it is possible to determine hydrogen with an error that is under 4% in the 100–650 ppm range, which is practically the entire αZr phase solubility range. The application of this method may be extended to determine the hydrogen fraction of the global concentration precipitated as hydrides in materials where a partition of the overall concentration between two phases exists, as Zr2.5%Nb or irradiated Zircaloy-4.

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