JOURNAL OF NUCLEAR MATERIALS 22 (1967) 304–310. © NORTH-HOLLAND PUBLISHING CO., AMSTERDAM

HYDROGEN SOLUBILITY IN ZIRCONIUM ALLOYS DETERMINED BY THERMAL DIFFUSION

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Received 3 January 1967

The terminal solid solubility (TSS) of hydrogen in Zircaloy-2 and Zr-2.5 wt % Nb annealed in the α and $(\alpha+\beta)$ regions has been determined in the temperature range 300° C to 515° C by making use of the thermal diffusion phenomenon. A temperature gradient impressed on a specimen initially uniformly hydrided, led to a solid solution plus hydride $(\alpha + \delta)$ region in the colder portion and a solid solution (α) in the warmer portion of the specimen. The TSS was taken to be the hydrogen concentration in the α region at the $\alpha/(\alpha + \delta)$ interface.

It was found that:

a. the TSS of both Zircaloy-2 and Zr-2.5 wt % Nb were given by $N = 1.99 \times 10^5 \exp(-9300/RT)$ ppm;

b. the TSS was the same for the two heat treatments used.

La limite de solubilité de l'hydrogène (TSS) dans la solution solide terminale du Zircaloy-2 et de l'alliage Zr-Nb à 2,5 % en poids de Nb recuit dans les domaines α et $(\alpha + \beta)$ a été déterminée dans l'intervalle de températures 300° – 515° C en utilisant les phénomènes de diffusion thermique. Un gradient de température imposé à un échantillon initialement hydruré de façon homogène conduit à une région biphasée $(\alpha + \delta)$ de solution solide + hydrure et à une solution solide α dans la portion la plus chaude de l'échantillon. La limite de solubilité à une température donnée a été prise comme étant la concentration en hydrogène dans la région α à l'interface $\alpha/(\alpha + \delta)$.

Les résultats montrent que

a. la courbe limite de solubilité de l'hydrogène à la fois dans le Zircaloy-2 et l'alliage Zr-Nb à 2,5 % en poids de Nb était donnée par

$$N = 1{,}99 \times 10^5 \exp(-9300/RT) \text{ ppm};$$

b. cette courbe de solubilité était la même pour les deux traitements utilisés.

Zur Bestimmung der Löslichkeitsgrenze von Wasserstoff in Zirkaloy-2 und einer Legierung von Zirkon mit 2,5 Gew.-% Niob im Temperaturbereich von 300–515° C wurden thermische Diffusionsmessungen durchgeführt. Die Proben waren im α- und im $(\alpha+\beta)$-Bereich geglüht worden. Wenn ein Temperaturgradient in einer vorher gleichmässig hydrierten Probe auftritt, so finden sich hinterher zwei Bereiche. In dem Probenbereich mit niedriger Temperatur tritt ein Mischkristall, gemischt mit dem Hydrid $(\alpha+\delta)$-Bereich auf, während in jenem Bereich der Probe, in dem die Temperatur höher war, lediglich ein α-Mischkristall auftritt. Als Löslichkeitsgrenze wurde jene Wasserstoffkonzentration angenommen, die an der Grenzfläche $\alpha/(\alpha+\delta)$ auftritt. Es wurde gefunden, dass die Löslichkeitsgrenze von Zirkaloy-2 und Zirkon mit 2,5 Gew.-% Niob durch die Formel wiedergegeben werden kann

$$N = 1{,}99 \times 10^5 \exp(-9300/RT) \text{ ppm}.$$

Diese Löslichkeitsgrenze gilt unabhängig von den beiden verschiedenen Wärmebehandlungen.

1. Introduction

Much of the work done on the hydrogen terminal solid solubility (TSS) in zirconium alloys below the eutectoid temperature was recently reviewed by Kearns [1]). Not included in the above were the investigations of Brown [2]) and Someno [3]) on zirconium, those of Daniel [4]) on Zircaloy-2 and Brown's [2]) work on zirconium-niobium alloys. Considerable discrepancy was observed in the results obtained by the various methods, particularly for the Zr-Nb alloys.

To simulate the conditions in reactor fuel sheathing the hydrogen TSS for Zircaloy-2 and Zr-2.5 wt % Nb was determined by making use of the thermal diffusion phenomenon. Specimens slow-cooled from the α region and

quenched from the $\alpha+\beta$ region were tested to determine the effect of heat treatment on hydrogen TSS.

2. Hydrogen redistribution under a temperature gradient

Under a temperature gradient the hydrogen flux in the α phase of the Zr-H system is given by Denbigh [5]) as

$$J=\{-DN/(RT)\}\{(RT\mathrm{d}\ln N/\mathrm{d}x)+ +(Q^*/T)(\mathrm{d}T/\mathrm{d}x)\}, \quad (1)$$

where D is the diffusion coefficient, N the hydrogen concentration, T the absolute temperature, R the gas constant and Q^* (positive for α-Zr) the heat of transport. Eq. (1) is readily solved for the steady state ($J=0$), giving the hydrogen distribution

$$N=N_0 \exp Q^*/(RT), \quad (2)$$

where N_0 is a constant depending on hydrogen content.

It has been shown [6]) that for an initially uniform hydrogen distribution exceeding TSS at the colder surface the transient hydrogen distribution has the form shown in fig. 1. A hydride layer forms at the colder surface. Adjoining this is an $\alpha+\delta$ region in which the hydrogen concentration increases linearly with time at all points, the rate of increase being an exponential function of the temperature. This leads to a discontinuity in hydrogen concentration between the $\alpha+\delta$ region and an α region in which the hydrogen distribution is approximately given by eq. (2). Equilibrium at the $(\alpha+\delta)/\alpha$ interface is assumed so that the hydrogen concentration N_1 in fig. 1 corresponds to TSS at the temperature T_1. The interface moves toward the colder surface at a rate dictated by hydrogen conservation so that eventually the $\alpha+\delta$ region disappears leaving the steady state hydrogen distribution.

The hydrogen redistribution under a temperature gradient thus provides a means of determining the TSS.

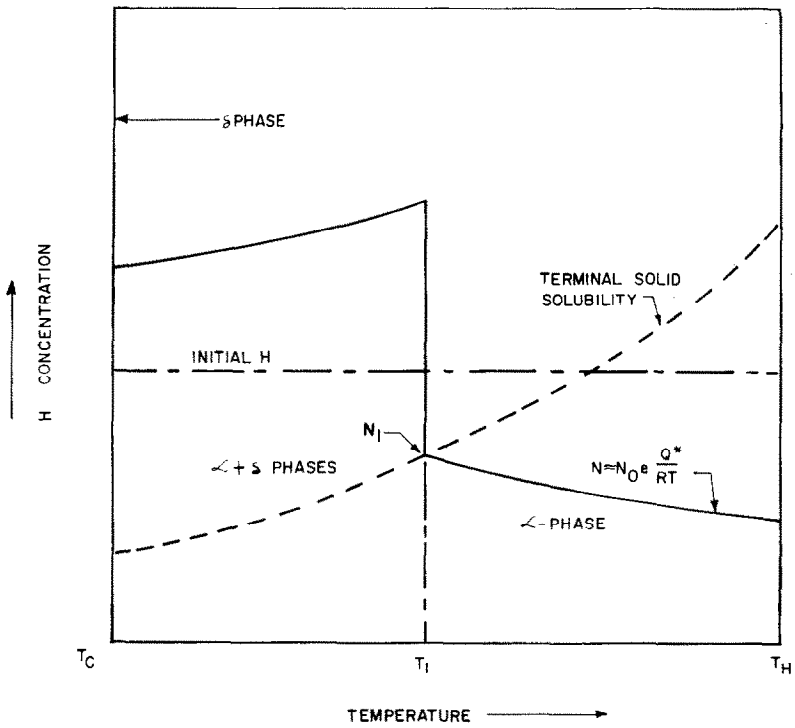

Fig. 1. Hydrogen redistribution under a temperature gradient.

3. Experimental procedure

3.1. Specimen preparation

The compositions of the two alloys used are given in table 1.

Table 1
Compositions of the alloys

	Zr-2.5 wt % Nb Alloying elements (wt %)	Zircaloy-2
Nb	2.50	—
Fe	—	0.14
Cr	—	0.08
Ni	—	0.06
Sn	—	1.55
	Impurities (ppm)	
Al	45	50
B	< 0.2	< 0.2
C	150	110
Cd	< 0.3	< 0.3
Co	< 5	< 5
Cr	120	—
Cu	35	< 25
Fe	850	—
Hf	45	65
Mg	< 10	< 10
Mn	15	< 10
Mo	15	< 10
N	60	35
Na	—	< 10
Ni	15	—
O	900	1400
Pb	10	< 5
Si	55	65
Sn	< 10	—
Ta	< 200	—
Ti	< 50	< 20
V	< 5	< 5
W	50	< 10
Zn	< 50	—
U	< 0.5	0.6

The specimens were machined cylinders 2 cm long and dia. 1.2 cm. Hydriding to concentrations at least twice that of the expected TSS was carried out by heating in hydrogen at 750° C in a Sievert's apparatus. The specimens were sealed off in individual evacuated quartz capsules and given one of the following heat treatments:

a. homogenized for 6 h in the α phase (600° C) and slowly cooled to room temperature or

b. as a. plus 1 h in the $\alpha+\beta$ region (750–850° C, depending on hydrogen concentration) followed by quenching in cold water.

3.2. Thermal diffusion anneal

The specimens were bolted between two stainless steel cylinders serving as heat reservoirs and the whole unit placed in a tube furnace having the desired temperature distribution.

Temperatures were measured with chromel-alumel thermo-couples pressed against the specimen end. To correlate temperature distribution to surface temperatures runs were made on a Zircaloy-2 dummy specimen which had thermocouples placed in radial holes meeting the axis at 0.2 cm intervals in addition to those at the surfaces. The radial temperature gradient was negligible. Temperature gradients were maintained at 25° C/cm to 65° C/cm for times ranging from 12 to 118 days, depending on specimen temperature.

The tests were carried out in air and the surface oxide formed served as a hydrogen barrier. After a run the oxygen rich surface layer was removed to a depth of 0.5 mm and the specimen was cut into parallel disks 1 mm thick. These were analyzed for hydrogen using the vacuum extraction technique.

The logarithm of the hydrogen concentration was plotted against the reciprocal of the absolute temperature as shown in fig. 2. The least squares fit of a straight line was obtained for the α region and extrapolated to the $\alpha/(\alpha+\delta)$ interface to yield the TSS.

3.3. Errors

The largest experimental error was found in measuring the interface temperature. To minimize this the lowest temperature gradient giving an acceptable rate of hydrogen redistribution was maintained. The maximum error in interface position is $\pm$ 0.75 mm (half

the thickness of disk plus saw cut). This corresponds to ± 2° C and ± 6° C for specimens having lowest and highest temperature gradients respectively. An additional ± 1° C accounts for the uncertainty in surface temperature. The mean deviation in hydrogen analysis was ± 3 %. The combined errors gave rise to an uncertainty in TSS of about ± 10 % at 300° C decreasing to ± 5 % at 500° C.

4. Results and discussions

Typical hydrogen distributions are shown in fig. 2. The transition between α and $\alpha+\delta$ phase regions is quite obvious.

The hydrogen TSS in Zr-2.5 wt % Nb is shown in fig. 3. The least squares fit of the data is given by $N = 1.55 \times 10^5 \exp(-8920/RT)$ ppm with a root-mean-square deviation of 5 ppm.

The hydrogen TSS in Zircaloy-2 is shown

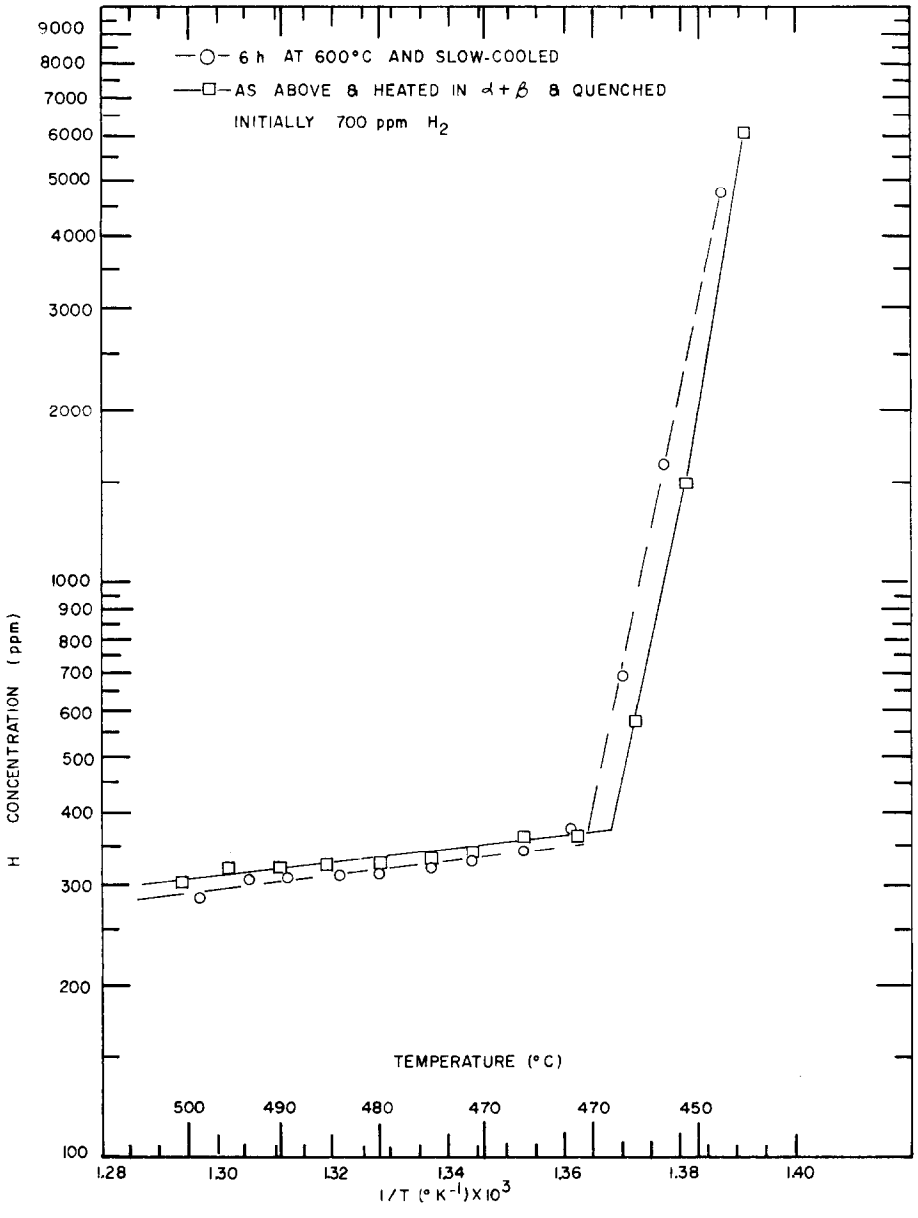

Fig. 2. Hydrogen distribution in Zircaloy-2 under a temperature gradient.

in fig. 4. The least squares fit of the data is given by $N = 2.88 \times 10^5 \exp(-9720/RT)$ ppm with a root-mean-square deviation of 5 ppm.

Over the temperature range investigated (300–515° C) the two sets of data can be represented by $N = 1.99 \times 10^5 \exp(-9300/RT)$ ppm with a root-mean-square deviation of 3 ppm. Combining most of the available data on hydrogen in zirconium Kearns [1]) obtained $N = 1.61 \times 10^5 \exp(-8950/RT)$ ppm. As seen in fig. 3 and 4 this is in excellent agreement with the present results. Thus small quantities of alloying element such as tin or niobium have negligible effect on the hydrogen solubility.

Heat treatment was found to have little influence on the hydrogen TSS. As seen in

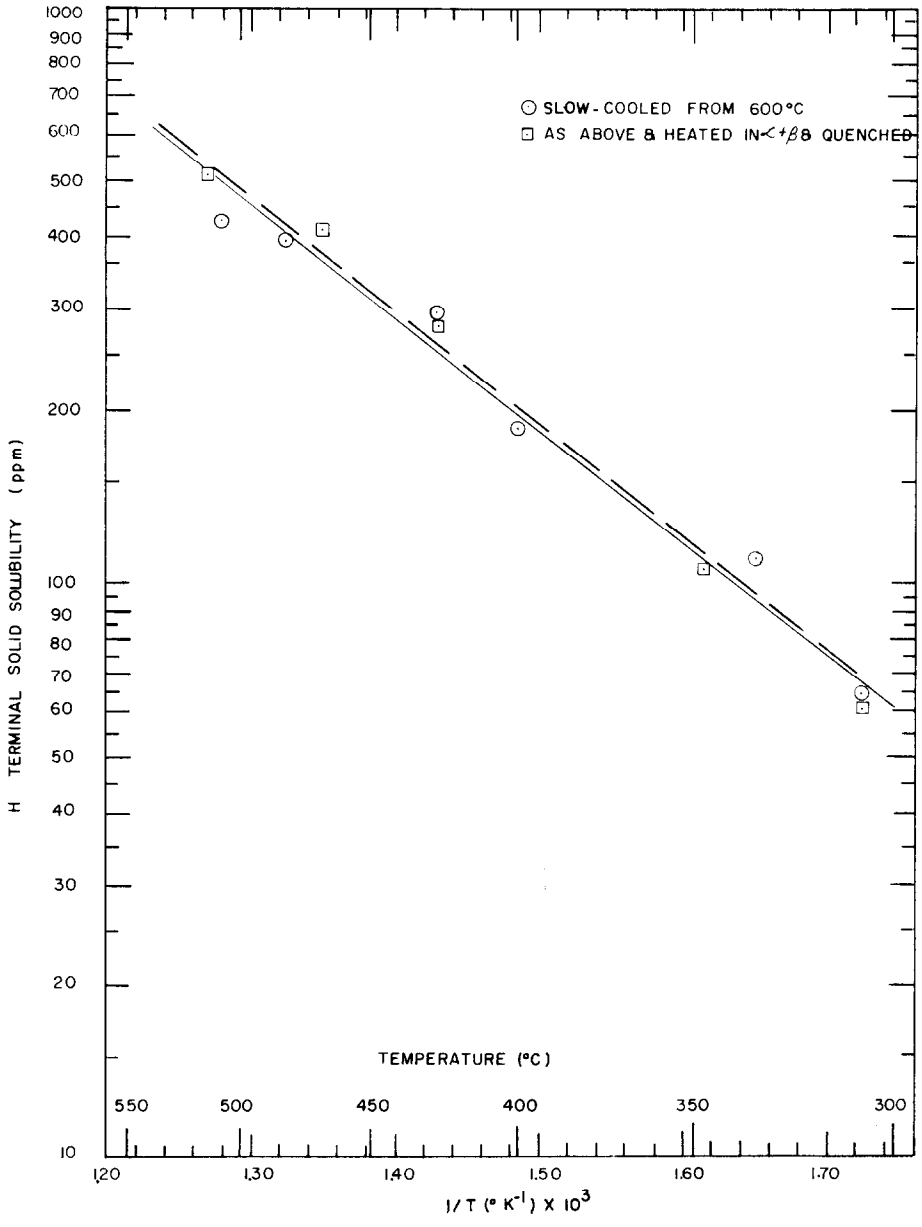

Fig. 3. Terminal solid solubility of hydrogen in Zr-2.5 wt % Nb. The continuous line is fitted to the experimental points while the broken line reproduces Kearns's data [1]) for zirconium.

figs. 3 and 4 the solubility data for samples slowly cooled from the α phase fall on the same line as data for samples quenched from the $\alpha+\beta$ region.

Based on a careful investigation of the pressure-temperature-concentration relationships in the Zr-H system Erickson [7]) has postulated the precipitation of a metastable hydride on cooling, which converts to a more stable hydride on reheating. There is then the possibility of obtaining several values for hydrogen TSS corresponding to either the metastable or stable phases, the value obtained depending on the experimental technique used. In the present investigation the specimens were hydrided, cooled to room temperature and

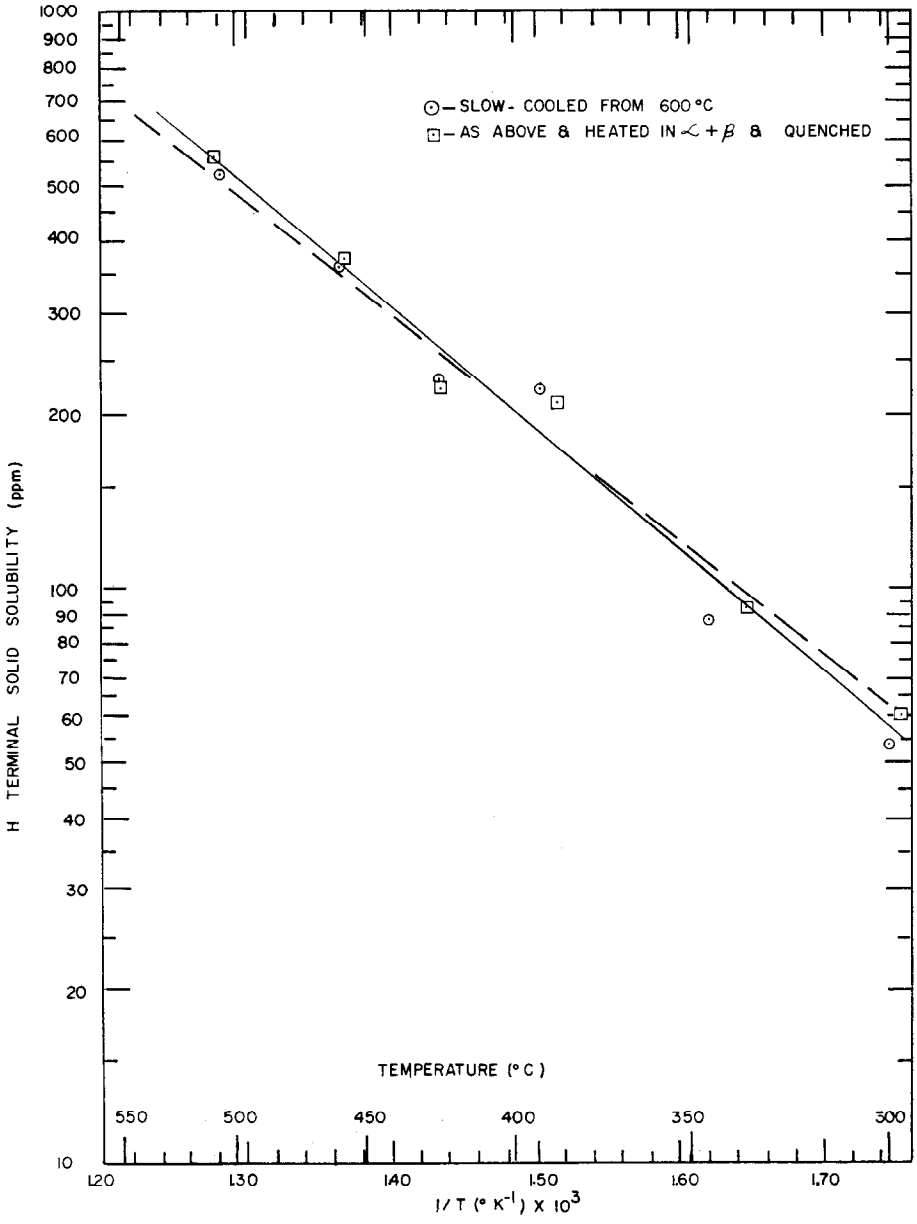

Fig. 4. Terminal solid solubility of hydrogen in Zircaloy-2. The continuous line is fitted to the experimental points while the broken line reproduces Kearns's data [1]) for zirconium.

reheated to the desired test temperature. The TSS obtained should therefore correspond to the stable hydride. Sawatzky [8]) previously obtained a somewhat higher TSS for hydrogen in Zircaloy-2 than the present value. However, he hydrided his specimens at the test temperature and therefore obtained the TSS corresponding to the metastable hydride.

Brown got values of hydrogen TSS in zirconium-niobium alloys three to four times higher than found in zirconium. He used a dilatometric method and during the course of his experiments apparently did not cool to less than 350° C. Thus, at least in part, his high values can be explained on the basis of a metastable hydride.

5. Conclusions

a. The hydrogen terminal solid solubility in Zircaloy-2 and Zr-2.5 wt % Nb obtained by a thermal diffusion method is given by $N = 1.99 \times 10^5 \exp(-9300/RT)$ ppm over the temperature range 300–515° C.

b. The TSS obtained by this method corresponds to the stable hydride.

c. Adding small amounts of tin or niobium to zirconium has little effect on the hydrogen TSS.

d. Heating Zircaloy-2 or Zr-2.5 wt % Nb in the α or $\alpha+\beta$ regions has a negligible effect on the hydrogen TSS.

Acknowledgements

Thanks are due to S. Jones and M. Duclos who assisted with the experimental work.

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