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Hydrogen (deuterium) bonding properties in ZrV_2D_x studied by SIMS and SNMS

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Abstract

Secondary ion mass spectrometry (SIMS) and secondary neutral mass spectrometry (SNMS) measurements on the Zr–V–H(D) system have been carried out to study the hydrogen bonding properties of the AB_2 Laves phase ZrV_2 in comparison to those of the pure components Zr and V. The SIMS spectra clearly show that Zr and V both keep their hydrogen bonding ability also in the Laves phase without clearly perceptible alterations. Only the hydrogen bonding character of Zr seems to be influenced a little, probably due to a weak electron transfer from zirconium.

Keywords: Zirconium–vanadium–deuterium; SIMS; SNMS; Cluster ions

1. Introduction

The fundamental aspects and the features of the secondary ion mass spectrometry (SIMS) and secondary neutral mass spectrometry (SNMS) for studying various properties of metal (alloy) hydrogen systems are described in detail elsewhere [1]. In this paper the special ability of SIMS to provide chemical information about metal hydrogen compounds is used by measuring the emission of hydrogen (deuterium) specific cluster ions.

From previous SIMS measurements on LaD_x, NiD_x, and $LaNi_5D_x$ [2] it is known, that LaD_x emits preferably negative LaD_n^- cluster ions ($0 \leq n \leq 5$) with high intensities, when bombarded by Ar^+ ions. The peaks exceed the positive ones by far. Such an intense mass peak pattern, which looks similar to that of negative metal oxide clusters [3], seems to be typical for saline hydrides. The LaD_2^- ion is the most intense one. In the negative SIMS spectrum of $LaNi_5D_x$ such a characteristic fingerprint is missed, only the ions La^- and LaD^- occur, but with small intensities. On the other hand, clear nickel–deuterium specific signals are detectable in the negative spectrum, which are observable in pure Ni only if high amounts of deuterium are implanted. The significant behavior of the AB_5 compound has been interpreted by an electron transfer from La to Ni in the intermetallic phase, whereby Ni becomes a hydride former under normal conditions, while La loses its ability to bind deuterium to a great extent. The characteristic cluster ion emissions are an excellent experimental and direct confirmation of band structure calculations [4,5].

Analogous measurements applied to the Zr–V–D system should show to what extent the hydrogen (deuterium) bonding properties of the pure metals are maintained or not in the ZrV_2 Laves phase.

2. Experimental

The SIMS- and SNMS-equipment but also the experimental conditions used in this investigation are identical to those mentioned elsewhere [1]. Since in this paper the main importance is attached to the comparison of mass spectra, the complete conditions for measuring the different samples were kept constant as far as possible. Only the sample preparation and hydrogen (deuterium) loading required some compromises. V and ZrV_2 could be gasvolumetrically loaded with deuterium under normal conditions without any problems. So clear deuterium specific SIMS signals could be obtained, which are nearly constant over a wide range of the bulk deuterium concentration [1]. Attempts to load Zr foils with deuterium in the same way failed. Zr could only electrochemically be loaded with H in a rather rough way up to concentrations that were sufficient for giving significant signals in the SIMS analysis. In this case H was chosen instead of D, normally used for SIMS experiments on metal hydrogen (deuterium) systems [6], because of additional experimental difficulties when applying D electrolysis. Since the solubilities of hydrogen

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(deuterium) in V, Zr, and ZrV_2 are different, but also since the SIMS- and SNMS-signals do not directly reflect the bulk concentration—because of ion bombardment induced hydrogen (deuterium) segregation effects [1]—the knowledge of exact absolute concentrations is irrelevant, but is also not necessary to reach the aim of the present investigation.

3. Results and discussion

In the following only representative mass peaks out of the measured spectra are presented since the main attention in this investigation is directed only to the specific metal hydrogen cluster ions which contain chemical information about the hydrides. The existence of five Zr isotopes [^{90}Zr: 51.46%; ^{91}Zr: 11.23%; ^{92}Zr: 17.11%; ^{94}Zr: 17.40%; ^{96}Zr: 2.8%] leads to a complex mass spectrum because of the superimposition of pure Zr isotope peaks with the manifold ones of the $ZrH(D)_n$ cluster ions. This has to be remembered when analysing the mass spectra. A logarithmic intensity scale is chosen, on principle, in order to cover the enormous detection range from 10–10^6 counts s^{-1} accessible to SIMS as well as to SNMS.

Fig. 1 shows typical mass peaks of positive and negative ions of the hydrogen (deuterium) loaded (white columns) Zr-, V-, and ZrV_2-samples, respectively, in each case together with the corresponding peaks from the unloaded (black columns) samples.

The yields of negative secondary ions are by far smaller than those of the positive ones, however, the presence and specific influence of hydrogen (deuterium) on the mass

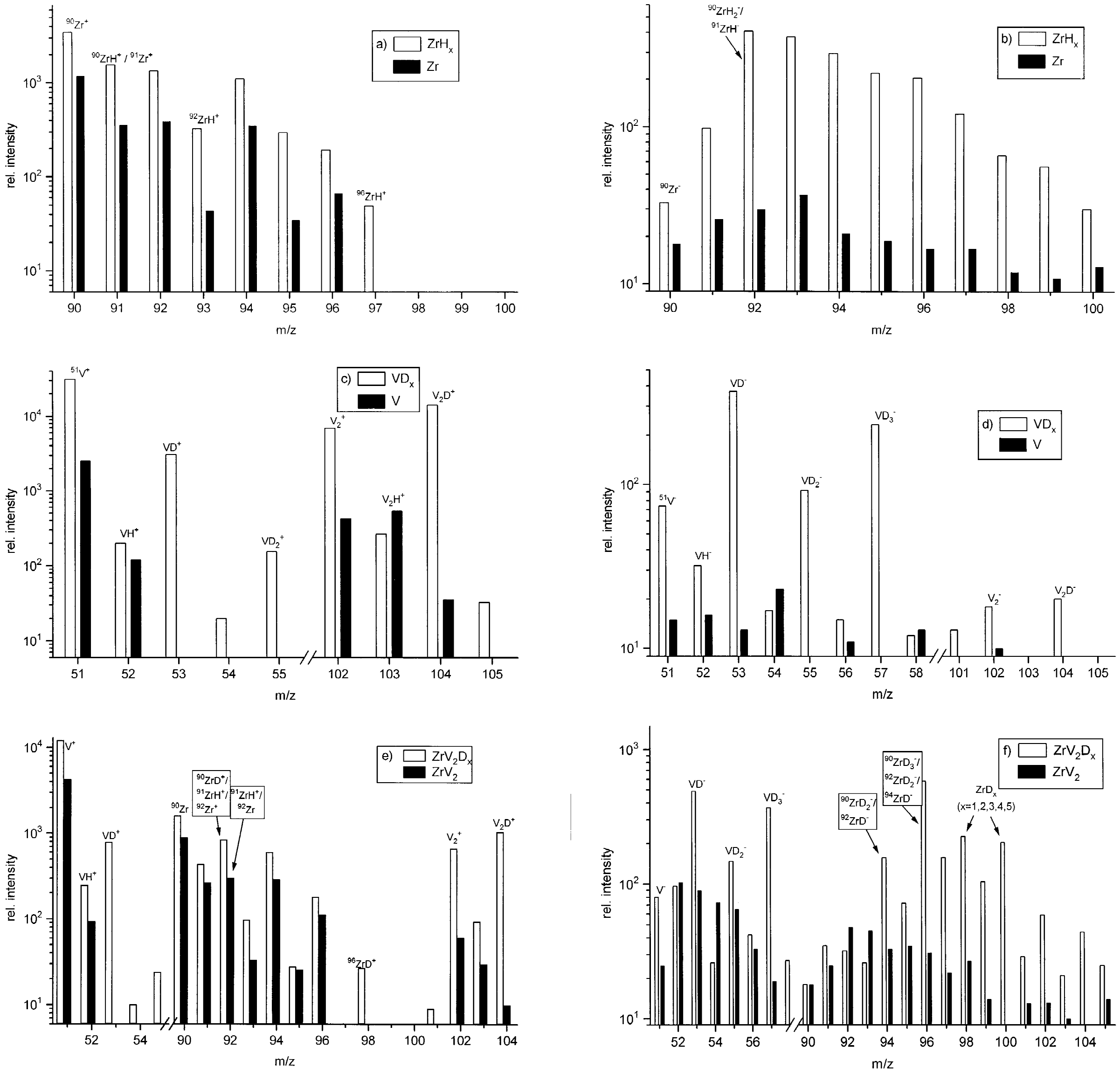

Fig. 1. Mass spectra of positive and negative secondary ions for hydrogen (deuterium) loaded (white columns) and unloaded (black columns) samples; (a) Zr, positive ions; (b) Zr, negative ions; (c) V, positive ions; (d) V, negative ions; (e) ZrV_2, positive ions; (f) ZrV_2, negative ions.

spectrum become quite clear in the negative spectra. The pure metal peaks (V^-, Zr^-) occur only with low intensities, compared to hydrogen (deuterium) cluster ions, thus in the case of Zr the contribution of the pure zirconium with its 5 isotopes to the measured mass peaks is small (7% at $m/z=91$), in contrast to the situation in the positive spectra (36% at $m/z=91$). Additionally, the yields of negative ions in hydrogen (deuterium) free samples are negligible in these mass ranges (Fig. 1(b), 1(d)). These facts facilitate the indication and interpretation of the mass peaks concerning the hydrogen (deuterium) influence.

In the case of Zr and ZrV_2, but also V residual hydrogen contents in the unloaded samples (Fig. 1(b), 1(d), 1(f)) give rise to a small emission of negative ions. Despite the influence of residual hydrogen, the hydrogen or deuterium uptake by the loading procedure is documented by the fact that the hydrogen (deuterium) specific peaks in the loaded samples are by far the dominating ones. Since the pattern of the Zr containing mass peaks is affected by the Zr isotope pattern the mass spectrum of Fig. 1(f) is resolved by calculation, considering the natural isotope abundance of Zr in order to get an isotope pure mass spectrum concerning zirconium, where the contributions of all other Zr isotopes than ^{90}Zr are eliminated. This modified mass spectrum is shown in Fig. 2(b) together with the ones of the pure metals V and ^{90}Zr. The intensities for the $^{90}ZrH_n^-$ peaks has been calculated from the peaks in Fig. 1(b), additionally, the $^{90}ZrH_n^-$ mass peaks are regarded as $^{90}ZrD_n^-$ ones, assuming, that the $^{90}ZrH_n^-$ pattern looks like the $^{90}ZrD_n^-$ one, as has been experimentally found for other metals [7]. The negative hydrogen (deuterium) cluster ion peak pattern of $^{90}ZrH(D)_n$- peaks is similar to that of LaD_x, though the peak heights are clearly smaller. This similarity might be an indication of at least a partly saline character of ZrD_x. A comparison of the mass peaks in Fig. 2(b) demonstrates impressively, that the hydrogen (deuterium) bonding characters of the pure metals are mostly maintained also in the AB_2 phase. Despite the relative small intensities for the negative ions the typical fingerprint spectra of the vanadium–deuterium and zirconium–deuterium cluster ions are repeated in the alloy. However, while in pure Zr the ZrD_2^- peak is the most intense one, the maximum in the pattern of the ZrV_2-sample shifts to ZrD_3^-. This shift to higher clusters can be taken as an indication for a part electron loss of zirconium in the alloy.

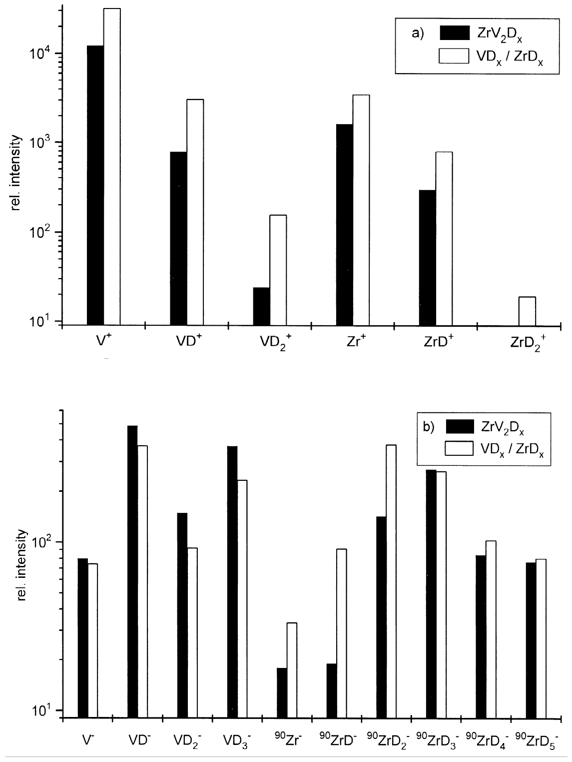

Fig. 2. Comparison of typical fingerprint spectra of deuterium loaded $^{90}ZrV_2$ with the ones from deuterium (hydrogen) loaded pure metals V and ^{90}Zr; (a) positive and (b) negative secondary ions.

As mentioned before, the positive secondary ion yields are higher by a factor of ten to hundred, however, the hydrogen (deuterium) presence is less obvious, at least at first sight. Due to the hydrogen induction effect, which favours the emission of positive ions [8], the ion yields—also for the pure metal ions—from the ZrH_x and ZrV_2D_x but especially for the VD_x sample are clearly higher than for the unloaded samples. Additionally, the mass peaks at $m/z=93$, 95 and 97 can only be ascribed to Zr–H–cluster ions. These are the peaks which are most enhanced in the hydrogen loaded Zr sample compared to the unloaded one. The positive mass spectra from the unloaded Zr, V and ZrV_2 samples indicate that the samples already contain small amounts of hydrogen, thus, the differences between the loaded and unloaded samples in the positive spectra are less pronounced.

The extraordinary mass peaks at $m/z=53$ (VD^+) and $m/z=104$ (V_2D^+) are a conclusive proof for the presence of deuterium in vanadium (Fig. 1(c)). The same is true for the deuterium loaded ZrV_2-sample (Fig. 1(e)). The detection of deuterium from the Zr–D cluster ions in the ZrV_2-sample is less evident in the positive spectrum, mainly due to the superimposition of Zr and Zr–D mass peaks, but also to the residual hydrogen in the ZrV_2 sample. However, as has been done for the negative spectra, the intensities for $^{90}ZrD_n^+$ cluster ions have been calculated from the mass spectra in Fig. 1(e) for the deuterium loaded sample. Fig. 2(a) shows the result. For comparison also the mass peaks from the pure elements V and ^{90}Zr (also calculated from the spectrum in Fig. 1(a)), each loaded with deuterium are plotted. Fig. 2(a) demonstrates that the mass peak pattern of the pure metals, both V and Zr, are maintained also in the positive spectrum of the alloy.

SNMS measurements confirm on the whole the SIMS results. The VD- and ZrD-fingerprint spectra of the pure elements coincide with the one from the alloy. However, the detection of cluster ions is limited, mainly due to the post-ionization process [9]. Clusters with more than three atoms are no longer observable, but also the yields of hydrogen (deuterium) specific cluster ions with only one hydrogen (deuterium) atom are clearly smaller than that of the pure single ion. As has already been discussed in the SIMS spectra, where the mass overlap of the pure zirconium isotopes with the zirconium–hydrogen(deuterium) cluster ions impedes the interpretation of the positive spectra, this effect is even more pronounced. The contribution of ^{91}Zr to the mass peak at $m/z=91$ is already 50%.

4. Conclusions

From SIMS-measurements on $LaNi_5D_x$ one must conclude that the hydrogen bonding to the components is quite different from that in the pure components. In ZrV_2 both metals nearly show the same high affinity to hydrogen (deuterium) as the pure metals. The shift in the emission of the ZrD_n^- cluster ions to higher deuterium contents seems to indicate a soft electron transfer from zirconium to vanadium.

References

[1] J. Scholz, H. Züchner, H. Paulus and K.-H. Müller, *these proceedings*.
[2] R. Dobrileit and H. Züchner, *Z. Naturforsch., 50A* (1995) 533.
[3] C. Plog, L. Wiedmann and A. Benninghoven, *Surf. Sci., 67* (1977) 565.
[4] W.E. Wallace, *J. Less-Common Met., 88* (1982) 141.
[5] M. Gupta, *J. Less-Common Met., 130* (1987) 219.
[6] H. Züchner and P. Kock, *Z. Physik. Chem. N.F., 164* (1989) 1165.
[7] H. Züchner and T. Brüning, *J. Alloys Comp., 231* (1995).
[8] H. Züchner, P. Kock and B. Hüser, *Fresenius Z. Anal. Chem., 329* (1987) 169.
[9] E. Stumpe, H. Oechsner and H. Schoof, *Appl. Phys., 20* (1979) 49.