SIMS Investigations on the SmCo₅Dₓ and LaNi₅Hₓ Systems

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Dedicated to Professor Dr. E. Wicke on occasion of his 80th birthday

Characteristic secondary ion emission patterns of several metal-hydrogen systems have been measured by SIMS to get information about the metal-hydrogen bonding and the structure of these systems. Results on SmCo₅Dₓ and LaNi₅Hₓ, and on H⁻D-loaded samples of the pure components are presented. The emission patterns of the secondary ions show a stronger bonding of hydrogen to Co and Ni than to Sm and La, although these transition metals, contrary to Sm or La, do not form stable hydrides under normal conditions. In these AB₅-compounds the transition metal seems to be transformed to a "hydride forming material" due to the presence of the rare earth element. The secondary ion emission patterns of the hydrogen loaded intermetallics are explained and compared to those of the hydrogen loaded pure components.

The similarity in the secondary ion emission patterns of the SmCo₅Dₓ and LaNi₅Hₓ systems points to a general characteristic of AB₅Hₓ materials.

Introduction

Intermetallic compounds [1] have proved to be very promising candidates for hydrogen storage. LaNi₅-based compounds are for instance used as hydrogen-electrodes in batteries, where they substitute the highly toxic cadmium [2]. Detailed information about the nature and strength of the metal hydrogen bond is therefore needed.

In this paper, SIMS-results on the hydrogen specific secondary ion yields of the AB₅ alloys SmCo₅ and LaNi₅, preloaded with hydrogen/deuterium, are discussed in consideration of the analogous results obtained for the pure components of the alloys, also loaded with hydrogen/deuterium.

Experimental

The measurements were carried out with a commercial SIMS setup equipped with a quadrupole-mass spectrometer (QMG 511 from Balzers Hochvakuum GmbH.). For a detailed description of the apparatus and the SIMS method see [3].

The pressure in the analyse-chamber was below 2·10⁻⁸ Pa, and the sample temperature was about 298 K. Primary ion bombardment was performed with Ar⁺-ions for the Sm, La, Ni and LaNi₅ samples and with D⁺-ions for the Co and SmCo₅ samples. The primary ion current density was 2·10⁻⁶ A/cm² with an energy of 3 keV. Bombardment with D⁺-ions was chosen because otherwise the deuterided Co and SmCo₅ samples would lose deuterium during bombardment. In order to get rid of surface contaminations, surface layers of about 80 nm were removed from the samples by ion sputtering before taking the spectra.

Hydrogen (deuterium) loading of the Ni, Co and SmCo₅ samples was done by H⁺(D⁺)-ion implantation since e.g. Ni or Co form only a thermodynamically instable hydride layer under normal conditions [4]. During the preloading process of the Ni, Co and SmCo₅ samples, about 10¹⁷ H⁺(D⁺) ions/cm² were implanted into the surface region of the sample. Deuterium loading of the Sm and La samples was carried out by applying a deuterium atmosphere of 1·10⁵ Pa and 872 K for Sm and 472 K for La, while the LaNi₅ sample was loaded electrochemically.

It is not possible to give exact values for the hydrogen (deuterium) concentrations in the sample region of interest for the SIMS experiments. But the relative intensities of the emitted ions depend only little on the absolute hydrogen (deuterium) concentration. Approximate concentrations are listed in Table 2.
Results and Discussion

In this investigation our main attention was directed to the emitted secondary metal-hydrogen (deuterium) cluster ions. Therefore only the corresponding ranges out of the mass spectra are presented and discussed in the following. In some cases the interpretation of the spectra became difficult due to the existence of more than one metal-isotope. This is true for Ni and especially for Sm (cf. Table 1), where overlaps of hydrogen containing mass peaks with pure isotope peaks had to be considered.

Because of the extreme range of intensities of different ion species, a logarithmic intensity scale was chosen for all mass spectra shown in the following. Additionally, the secondary ion intensities have been given with respect to the intensity of the lightest isotope of the element, if not stated otherwise. The standardization factors are given in the figures. This standardization enables a better comparison of different samples, especially in cases where the total secondary ion emission intensity differs strongly from sample to sample.

a) The Systems SmDₙ, CoDₙ and SmCo₅Dₙ

Sm reacts with hydrogen to a salt like hydride, which results in a high negative charge density in the vicinity of the hydrogen atom. Sm possesses a wide range of isotopes from mass 144 to 154 (see Table 1) with ¹⁵²Sm and ¹⁵⁴Sm as the main components. This isotope spectrum leads to a superposition of mass peaks with different deuterium content. For example ¹⁵⁰SmD₂, ¹⁵₂SmD, and ¹⁵⁴Sm appear at the same m/e value in the spectrum. Therefore the most significant SmDₓ signals should be found at mass 156 (¹⁵⁴SmD) and the following masses since these signals do not overlap with signals of non-deuterated Sm isotopes (Figs. 1a and 1b). The positive partial mass spectrum of SmCo₅Dₙ in Fig. 1a almost reflects the normal distribution of the natural Sm isotopes. Only a little deuterization becomes obvious in the ¹⁵⁴SmD peak at mass 156. In contrast to this, the SmD⁺ peak of the SmDₙ sample has the highest intensity of all SmDₓ clusters. This clear difference in the emission behaviour of SmDₓ and SmCo₅Dₙ samples becomes even more obvious in the negative cluster ion yields in Fig. 1b, while for SmCo₅Dₙ no clear SmD⁻ signal is observed at all, strong SmD₂⁻ signals occur for the SmDₙ sample with x ranging up to 4. This can be explained by the negative charge of deuterium in SmDₙ, leading to the emission of the negative cluster ions with intensities which are more intense than the positive ones, when applying identical bombarding conditions. The different emission behaviour of SmDₙ on the one hand and SmCo₅Dₙ on the other hand with regard to SmDₓ-specific secondary ions indicates that deuterium is less bonded to Sm in the alloy. The statement implies that deuterium should be more bonded to Co. Indeed, the corresponding secondary ion yields of Co-Dₓ cluster ions confirm this statement.

The positive CoDₓ cluster ion emission pattern (Fig. 2a) is nearly identical for the SmCo₅Dₙ and CoDₙ samples; only the CoD signal at mass 61 shows a slightly higher intensity for the SmCo₅Dₙ sample. This behaviour is quite similar to that of the negative secondary ion emission (Figure 2b). In this case, however, the CoD⁻ and CoD₂⁻ intensities are higher for the SmCo₅Dₙ sample. This similarity in the emission behaviour of both samples regarding the CoD cluster ions indicates that there is no remarkable difference between the Co-D bond in CoDₙ and in SmCo₅Dₙ, but an increased electronic charge density for the CoDₓ cluster ions in SmCo₅Dₙ.

Table 1. The natural isotope distribution of the relevant elements.

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass</th>
<th>Isotope fraction in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm</td>
<td>144</td>
<td>3.09</td>
</tr>
<tr>
<td></td>
<td>147</td>
<td>14.97</td>
</tr>
<tr>
<td></td>
<td>148</td>
<td>11.24</td>
</tr>
<tr>
<td></td>
<td>149</td>
<td>13.83</td>
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<tr>
<td></td>
<td>150</td>
<td>7.44</td>
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<tr>
<td></td>
<td>152</td>
<td>26.72</td>
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<tr>
<td></td>
<td>154</td>
<td>22.71</td>
</tr>
<tr>
<td>Co</td>
<td>59</td>
<td>100</td>
</tr>
<tr>
<td>La</td>
<td>138</td>
<td>0.089</td>
</tr>
<tr>
<td></td>
<td>139</td>
<td>99.911</td>
</tr>
<tr>
<td>Ni</td>
<td>58</td>
<td>67.88</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>26.23</td>
</tr>
<tr>
<td></td>
<td>61</td>
<td>1.19</td>
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<tr>
<td></td>
<td>62</td>
<td>3.66</td>
</tr>
<tr>
<td></td>
<td>64</td>
<td>1.08</td>
</tr>
</tbody>
</table>

¹ Note the logarithmic scale with ¹⁵⁴SmD at mass 156 having an intensity less than 10% compared to ¹⁵⁴Sm.
² The intensities in Fig. 1b are not normalized due to the fact that there is no structure in the mass spectrum because of a high background. The high background is typical, unfortunately, to all negative spectra of the SmCo₅Dₙ samples. This fact impedes the interpretation of the corresponding negative spectra partially.
The comparison of the emission of the negative \( \text{Co}_2\text{D}_x \) cluster ions in Fig 3 b also shows a good agreement for the samples. Unfortunately, no \( \text{Co}_2\text{D}_x^+ \) clusters could be found in the spectrum of \( \text{SmCo}_5\text{D}_x \), caused, probably, by the higher electron density near the Co sites, which leads to a lower emission probability of positive Co-containing clusters; so, in this case a comparison between the two samples is impossible.

The fact that in \( \text{SmCo}_5\text{D}_x \) only small amounts of deuterium are detected as \( \text{SmD}_x \), together with the similarity in the secondary ion emission patterns for the \( \text{CoD}_x \) and \( \text{SmCo}_5\text{D}_x \) samples concerning the \( \text{CoD}_x \) cluster ions (Figs. 2 a and b) proves that deuterium in \( \text{SmCo}_5\text{D}_x \) is more associated to Co than to Sm.

If this statement is characteristic for \( \text{AB}_5 \) materials, similar results should be observable for the corresponding \( \text{LaNi}_5\text{H}_n \) system.

b) The systems \( \text{LaD}_n, \text{NiH}_n, \) and \( \text{LaNi}_5\text{H}_n \)

Lanthanum forms hydrides with a mainly ionic character; the negative charge density is locally increased at the deuterium site [5, 6]. Lanthanum possesses two isotopes, an abundant one at mass 139 and a rare one at mass 138. Therefore only \( ^{139}\text{La} \) will be discussed in the emission pattern of \( \text{LaD}_n \) and \( \text{LaNi}_5\text{H}_n \) and the measured peaks were standardized relative to the \( ^{139}\text{La} \) intensity.

Figures 4 a and 4 b show the positive and negative emission patterns of La-containing cluster ions in the \( \text{LaD}_n \) and \( \text{LaNi}_5\text{H}_n \) samples. For an easier comparison of the emission patterns of deuterium and hydrogen charged samples, and assuming that the isotope...
effect on the emission behaviour can be neglected, the
mass scale for LaNi$_5$H$_n$ was changed high-handedly in such a way that LaH appears at the same mass than
LaD. The secondary ion yields for LaD$^+$ and LaD$_2^+$ are higher for the LaD$_n$ sample than LaH$^+$ and LaH$_2$ for the LaNi$_5$H$_n$ sample (Figure 4a). The same trend can be observed in the negative spectra. The LaNi$_5$H$_n$ sample yields a low LaH$^-$ emission, while high intensities of LaD$_x$ clusters occur for the LaD$_n$ sample with $x$ up to 4. LaD$_2^-$ shows the strongest signal, and even clusters with higher D-contents, as for example LaD$_4$ at mass 147, are emitted in great quantities. The same emission behaviour was also observed for the SmD$_n$ and SmCo$_5$D$_n$ samples (see before).

The emission patterns of Ni containing cluster ions (Figs. 5a and b) are also quite similar to that of Co-containing clusters (Figs. 2a and b). The natural isotope distribution is well reflected in Fig. 5a. Only a negligible intensity of hydrogen-containing clusters is found for both samples. In contrast to this, a strong emission of hydrogen-containing clusters is observed in the negative spectra (Fig. 5b), where $^{58}$NiH$_2$ is detected as the highest signal in the spectrum, like CoD$_2^-$ in CoD$_n$ and SmCo$_5$D$_n$.

The emission of Ni$_2$-containing clusters from NiH$_n$ and LaNi$_5$H$_n$ is also quite similar to that of Co$_2$-containing clusters, as discussed before. Figure 6a shows almost the same emission characteristic for both samples with $^{58}$Ni$_2$H$^+$ at mass 117 as the highest signal. The reason for the relatively high intensity at mass 119 is not due to a strong emission of Ni$_2$H$_3$ cluster ions but rather to the emission of mixed $^{60}$Ni$^{58}$NiH cluster ions. The emission pattern of the negative clusters is quite analogous to the positive
ones, with \( \text{Ni}_2\text{H}^- \) being the cluster with the highest emission intensity \(^4\).

The good agreement between the emission patterns of \( \text{NiH}_x \) and \( \text{LaNi}_5 \text{D}_x \) regarding the secondary ion yields of Ni-specific ions points to the equivalence of the Ni-H bond in both samples. This is in good accord­ance with investigations of Wallace et al., who found similar d-band structures for Ni and \( \text{LaNi}_5 \), from which the authors concluded that the hydrogen bond in \( \text{LaNi}_5 \text{H}_x \) should be similar to that in Ni \([7, 8]\).

On comparing the absolute intensity ratios of the most significant positive and negative cluster ions in Tables 2a and b, differences in the emission behaviour of the samples become evident. The deuterated rare earth metals show strong emissions of negative D containing clusters, which becomes even more evident by

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\(^4\) Fig. 6b was not standardized to the \(^{58}\text{Ni}_2\) intensity at mass 116 because there is no clearly detectable \(^{58}\text{Ni}_2\) signal for the \( \text{NiH}_x \)-sample.

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like the hydrided single components do. In both systems only small intensities of rare earth-hydride clusters occur, while intense emissions are observed for transition metal-hydride clusters mainly as negative ions. This leads to the conclusion that hydrogen is preferable bonded to the transition metal in form of a mainly negatively charged Me-Hx-cluster.

The measurements presented in this paper show directly that the transition metal becomes the "hydride forming species" by the presence of an (electropositive) rare earth metal, which greatly determines the storage capacity and other characteristics of AB5-hydrogen systems. The rare earth metal itself loses the capability to form a hydride. The SIMS results do not allow, at that moment, a decision whether electronic or structural (e.g. lattice expansion) effects are responsible for the preferential bonding of hydrogen to the transition metal in the alloys.

The new hydrogen implantation technique used for sample preparation yields high hydrogen contents even in samples which are not to be charged under normal conditions by other conventional methods. This technique enables SIMS measurements at significantly high hydrogen concentrations for almost all materials. No differences between the emission behaviour for samples which were loaded by hydrogen implantation and samples which were loaded gas volumetrically could be observed, as has also been shown for the Nb-H/D system [9].

References: