SIMS Investigations on the $SmCo_5D_n$ and $LaNi_5H_n$ 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 $SmCo_5D_n$ and $LaNi_5H_n$, 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 AB_5-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 $SmCo_5D_n$ and $LaNi_5H_n$ systems points to a general characteristic of AB_5H_n materials.

Introduction

Intermetallic compounds [1] have proved to be very promising candidates for hydrogen storage. $LaNi_5$-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 AB_5 alloys $SmCo_5$ and $LaNi_5$, 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 $2 \cdot 10^{-8}$ Pa, and the sample temperature was about 298 K. Primary ion bombardment was performed with Ar^+-ions for the Sm, La, Ni and $LaNi_5$ samples and with D^+-ions for the Co and $SmCo_5$ samples. The primary ion current density was $2 \cdot 10^{-6}$ A/cm^2 with an energy of 3 keV. Bombardment with D^+-ions was chosen because otherwise the deuterided Co and $SmCo_5$ 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 $SmCo_5$ 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 $SmCo_5$ samples, about 10^{17} $H^+(D^+)$ ions/cm^2 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 $1 \cdot 10^5$ Pa and 872 K for Sm and 472 K for La, while the $LaNi_5$ 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.

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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 SmD_n, CoD_n and $SmCo_5D_n$

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 ^{152}Sm and ^{154}Sm as the main components. This isotope spectrum leads to a superposition of mass peaks with different deuterium content. For example $^{150}SmD_2$, ^{152}SmD, and ^{154}Sm appear at the same m/e value in the spectrum. Therefore the most significant SmD_x signals should be found at mass 156 (^{154}SmD) 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 $SmCo_5D_n$ in Fig. 1a almost reflects the normal distribution of the natural Sm isotopes. Only a little deuteration becomes obvious in the ^{154}SmD peak at mass 156[1]. In contrast to this, the SmD^+ peak of the SmD_n sample has the highest intensity of all SmD_x clusters. This clear difference in the emission behaviour of SmD_x and $SmCo_5D_x$ samples becomes even more obvious in the negative cluster ion yields in Fig. 1b[2], while for $SmCo_5D_n$ no clear SmD_x-signal is observerd at all, strong SmD_x-signals occur for the SmD_n sample with x ranging up to 4. This can be explained by the negative charge of deuterium in SmD_n, 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 SmD_n on the one hand and $SmCo_5D_n$ on the other hand with regard to SmD_x-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-D_x cluster ions confirm this statement.

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

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

The positive CoD_x cluster ion emission pattern (Fig. 2a) is nearly identical for the $SmCo_5D_n$ and CoD_n samples; only the CoD signal at mass 61 shows a slightly higher intensity for the CoD_n sample. This behaviour is quite similar to that of the negative secondary ion emission (Figure 2b). In this case, however, the CoD^- and CoD_2^- intensities are higher for the $SmCo_5D_n$ 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 CoD_n and in $SmCo_5D_n$, but an increased electronic charge density for the CoD_x cluster ions in $SmCo_5D_n$.

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[1] Note the logarithmic scale with ^{154}SmD at mass 156 having an intensity less than 10% compared to ^{154}Sm.

[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 $SmCo_5D_n$ samples. This fact impedes the interpretation of the corresponding negative spectra partially.

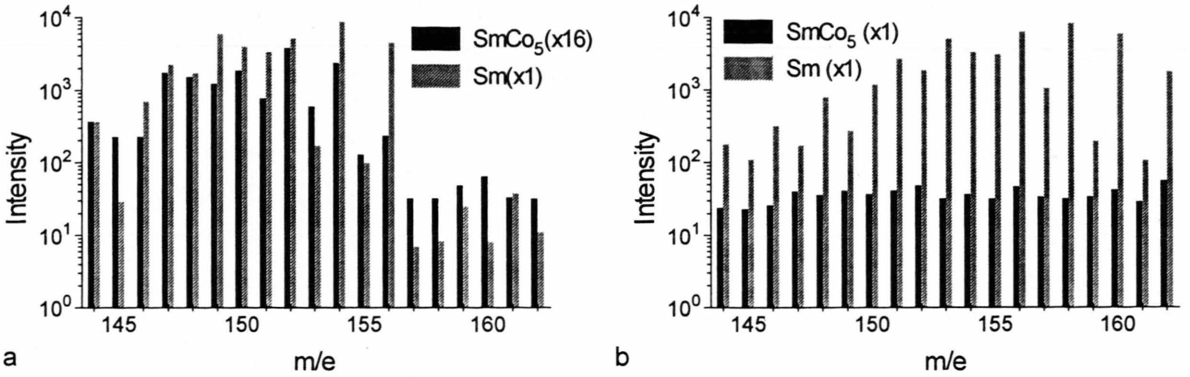

Fig. 1. Intensities of the standardized positive (a) and negative (b) secondary Sm and SmD_x ions.

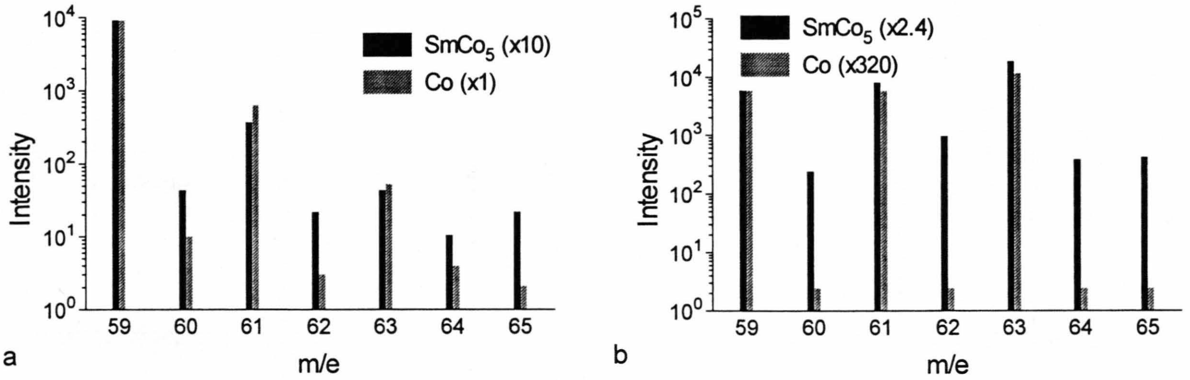

Fig. 2. Standardized intensities of the positive (a) and negative (b) secondary Co and CoD_x ions.

The comparison of the emission of the negative Co_2D_x cluster ions in Fig 3b also shows a good agreement for the samples. Unfortunately, no $Co_2D_x^+$ clusters could be found in the spectrum of $SmCo_5D_n$[3], caused, probably, by the higher electron density near the Co sites, which leads to a lower emission probability of positive Co_2-containing clusters; so, in this case a comparison between the two samples is impossible.

The fact that in $SmCo_5D_n$ only small amounts of deuterium are detected as SmD_x, together with the similarity in the secondary ion emission patterns for the CoD_n and $SmCo_5D_n$ samples concerning the CoD_x cluster ions (Figs. 2a and b) proves that deuterium in $SmCo_5D_n$ is more associated to Co than to Sm.

If this statement is characteristic for AB_5 materials, similar results should be observable for the corresponding $LaNi_5H_n$ system.

b) The systems LaD_n, NiH_n, and $LaNi_5H_n$

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}La will be discussed in the emission pattern of LaD_n and $LaNi_5H_n$ and the measured peaks were standardized relative to the ^{139}La intensity.

Figures 4a and 4b show the positive and negative emission patterns of La-containing cluster ions in the LaD_n and $LaNi_5H_n$ samples. For an easier comparison of the emission patterns of deuterium and hydrogen charged samples, and assuming that the isotope

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[3] The intensities in Fig. 3a are not standardized due to the fact that no clear mass dependence of the intensity for Co_2^+ containing clusters in $SmCo_5D_n$ could be observed (see Footnote 1).

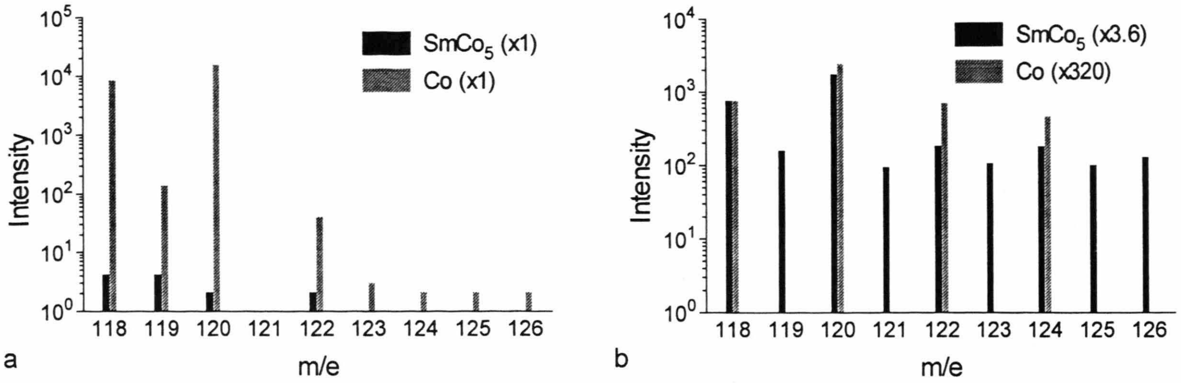

Fig. 3. Intensities of the positive (a) and standardized negative (b) secondary Co_2 and Co_2D_x ions.

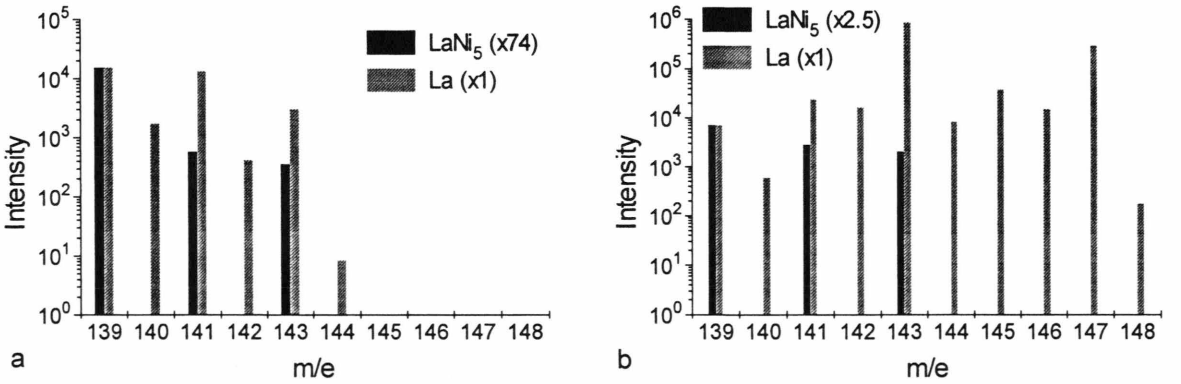

Fig. 4. Standardized intensities of the positive (a) and negative (b) secondary La, LaH_x, and LaD_x ions with a "changed" mass scale for H containing clusters in $LaNi_5$.

effect on the emission behaviour can be neglected, the mass scale for $LaNi_5H_n$ 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 $LaNi_5H_n$ sample (Figure 4a). The same trend can be observed in the negative spectra. The $LaNi_5H_n$ sample yields a low LaH_x^- 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 $SmCo_5D_n$ 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 $SmCo_5D_n$.

The emission of Ni_2-containing clusters from NiH_n and $LaNi_5H_n$ is also quite similar to that of Co_2-containing clusters, as discussed before. Figure 6a shows almost the same emission characteristica for both samples with $^{58}Ni_2H^{\pm}$ 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_2H_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

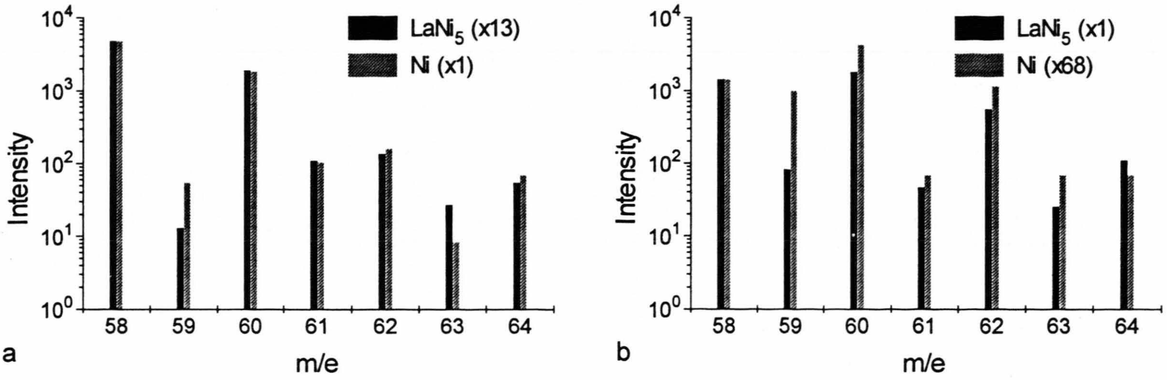

Fig. 5. Standardized intensities of the positive (a) and negative (b) secondary Ni and NiH_x ions.

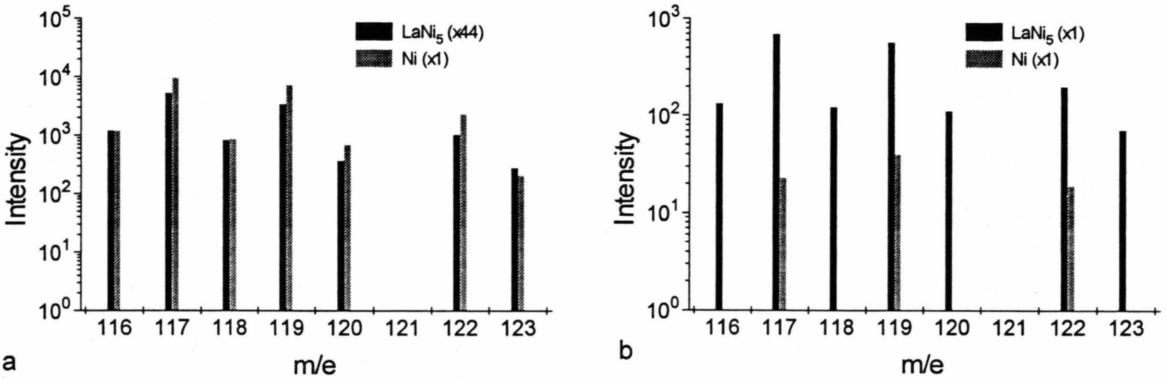

Fig. 6. Intensities of the standardized positive (a) and negative (b) secondary ions Ni_2 and Ni_2H_x.

ones, with Ni_2H^- being the cluster with the highest emission intensity[4].

The good agreement between the emission patterns of NiH_n and $LaNi_5D_n$ 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 $LaNi_5$, from which the authors concluded that the hydrogen bond in $LaNi_5H_n$ 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 the intense emission of SmD_4^- and LaD_4^- without any corresponding ion in the positive spectrum (see Figs. 1 and 4). The hydrided (deuterided) transition metals show the opposite behaviour; the emission of positive ions dominates the spectra with almost no emission of negative ions.

This emission behaviour is reversed in the alloys, where large quantities of H(D) containing negative transition metal cluster ions appear, while there are almost no D containing negative rare earth cluster ions. This shows quite well the changes in charge distribution from the hydrided (deuterided) pure components to the hydrided (deuterided) alloys.

Conclusions

The systems $SmCo_5D_n$ and $LaNi_5H_n$ show quite similar emission patterns in SIMS-measurements, just

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[4] Fig. 6b was not standardized to the $^{58}Ni_2$ intensity at mass 116 because there is no clearly detectable $^{58}Ni_2$ signal for the NiH_n-sample.

Table 2. Approximate D(H) concentrations in the samples, and intensity ratios of positive and negative cluster ions. a) for the systems SmD_n, CoD_n and $SmCo_5D_n$; b) for the systems LaD_n, NiH_n and $LaNi_5H_n$.

a	Concentration	Co^+/Co^-	CoD_2^+/Co_2^-	Co_2D^+/Co_2D^-	Sm^+/Sm^-	SmD^+/SmD^-
SmD_n	$n \approx 2.5$				15	9
CoD_n	$n \approx 0.4$	1207	85	2019		
$SmCo_5D_n$	$n \approx 0.1$	0.15	0.004	0.02	65	10

b	Concentration	Ni^+/Ni^-	NiH_2^+/NiH_2^-	Ni_2H^+/N_2H^-	La^+/La^-	LaD^+/LaD^-
LaD_n	$n \approx 2.5$				2.2	0.56
NiH_n	$n \approx 0.6$	227	>54	411		
$LaNi_5H_n$	$n \approx 0.05$	0.26	0.004	0.17	65	5.3

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-H_x-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 characteristica of AB_5-hydrogen systems. Ther 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 gasvolumetrically could be observed, as has also beeen shown for the Nb-H/Dsystem [9].

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