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A secondary ion mass spectrometry study of hydrogen interaction with $Nd_2(Fe/Co)_{14}B$

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Abstract

For studying hydrogen binding and electronic surface effects in the metal hydrogen system $Nd_2(Fe/Co)_{14}B$ SIMS (secondary ion mass spectrometry) is applied to hydrogen free and in situ hydrogenated alloys. Hydrogenation under UHV conditions is achieved by use of D_2^+ ion implantation during SIMS measurements. Specific information on hydrogen surface binding characteristics and hydrogen-induced electronic effects are obtained by analyzing secondary ion cluster pattern from positive and negative SIMS spectra. The SIMS data confirm and complete our XPS results. They show a significantly different behavior of the Fe- and Co-alloy against hydrogen with respect to secondary ion emission. The cluster ion emission pattern of $Nd_2Fe_{14}B$ primarily reflects the properties of rather isolated elements, while the situation in $Nd_2Co_{14}B$ points to a more stable chemical bonding between the alloy components. This observation became obvious also in XPS investigations [D. Lebiedz, H. Züchner, O. Gutfleisch, Chem. Mater., in press] as well as the HDDR process [O. Gutfleisch, I.R. Harris, J. Phys. D: Appl. Phys. 29 (1996) 2255]. Hydrogenation leads to changes of the secondary ion cluster intensities and composition concerning Nd containing cluster ions, which again emphasizes the high significance of the lanthanoid for hydrogen binding. Additionally, the SIMS data suggest that the kind of transition metal (Fe and Co) plays an essential role for the first step of hydrogen uptake, the hydrogen dissociation at the metal surface. In that respect, Fe in $Nd_2Fe_{14}B$ has turned out to be catalytically more effective than Co.

Keywords: Hydrogen in intermetallics; Magnetic properties; HDDR-process; SIMS

1. Introduction

The system $Nd_2Fe_{14}B$ can be hydrogenated under moderate conditions of 1 bar hydrogen pressure and 420 K [2]. An unusual behavior is observed during further heat treating in hydrogen atmosphere. The alloy disproportionates into NdH_2, α-Fe and Fe_2B at temperatures above 920 K [3,4]. At temperatures higher than 1370 K the disproportionated mixture recombines to $Nd_2Fe_{14}B$ with high magnetic coercivity and some anisotropy [5]. This process referred to as HDDR (hydrogen–disproportionation–desorption–recombination [6,7]) is technically applied to produce bonded and hot pressed magnets with special properties. A partial substitution of Fe by Co in $Nd_2(Fe_xCo_{1-x})B$ results in an increase of hydrogenation and disproportionation temperatures as well as an increase of magnetic anisotropy [8]. These phenomena have been studied by TEM [9] and XPS [1] to get further information on the hydrogenation behavior of these alloys in general and the characteristics of the HDDR process with regard to hydrogen-induced electronic and structural changes and the effect of Fe substitution by Co. Zhang et al. studied the magnetic behavior of $R_2Fe_{14}B$ and $R_2Co_{14}B$ hydrides (R=lanthanoid) in earlier works [10,11].

In the present work SIMS (secondary ion mass spectrometry) is applied to analyze further hydrogen surface effects in the alloys $Nd_2(Fe/Co)_{14}B$ and in particular significant differences in the hydrogen binding characteristics of the Fe- and Co-system. As reference data SIMS spectra of pure Nd, Fe and Co have been measured and compared to those of the alloys. Hydrogenation under UHV condition is achieved by D_2 absorption/implantation from the gas phase during SIMS measurements. For that purpose the analysis chamber of the spectrometer is partially deuterium filled to a pressure of $p(D_2)=5\times10^{-3}$

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Pa.[1] The lattice dilatation at the metal surface induced by Ar ion bombardment during SIMS analysis results in a deuterium enrichment in the near surface region and a reduced deuterium desorption pressure [12]. Using this technique deuterium binding characteristics can be investigated under well defined conditions by studying metal-deuterium cluster ion emission almost completely uninfluenced by oxygen residual gas contamination. In earlier studies [13] hydrogen location in the crystal lattice of $Nd_2Fe_{14}B$ was studied by neutron diffraction and the change in magnetism was attributed to a change in the shortest iron–iron distance upon hydrogenation.

2. Experimental

2.1. Preparation of Nd–Fe–B alloys

The $Nd_2(Fe_xCo_{1-x})_{14}B$ ($x=1$, 0.75, 0.5, 0) samples have been prepared by the IFW Dresden by inductively coupled melting of elemental Nd, Fe, Co, FeB, CoB (purities 99.9%) with subsequent homogenization at 1323 K for 96 h. For details and control XRD measurements see [14]. From this raw material pieces of 0.2 cm^2 and 0.2 cm thickness have been cut with an isomet 4000 machine (Wirtz-Bühler) using a diamond-coated cutting-off wheel with high rotation speed. These slices were polished using diamond paste and afterwards carefully degreased in acetone and methanol using ultrasonic cleaning.

2.2. SIMS measurements

All SIMS measurements were performed in a Balzers/Physical Electronics spectrometer. Spectra of deuterated samples alloys were obtained after filling the analysis chamber of the SIMS spectrometer up to a pressure of $p(D_2)=5\times10^{-3}$ Pa. Ar ion sputtering was performed at a pressure of $p(Ar)=10^{-4}$ Pa (dynamic SIMS mode).

3. Results and discussion

The SIMS data are analyzed with the aim to detect the function of the different alloy components regarding surface hydrogen adsorption and subsequent hydrogen binding in the alloy. The comparison of secondary ion cluster emission pattern of $Nd_2Fe_{14}B$ and $Nd_2Co_{14}B$ indicates that the Co alloy seems to be the more stable one. The spectra of the Fe alloy show clear characteristics of the isolated alloy components Nd and Fe as confirmed by reference measurements of pure Nd and Fe. The ratio of secondary ion intensities $I(Nd^+)/I(NdFe^+)$ in $Nd_2Fe_{14}B$ is significantly higher than $I(Nd^+)/I(NdCo^+)$ in $Nd_2Co_{14}B$ and for the latter alloy the intensity of negative Me_x^- cluster (Me=Fe,Co) is considerably higher than for $Nd_2Fe_{14}B$. Both aspects point to a stronger and more polarized Nd–Me bonding for Me=Co. The contrast between the Fe and Co alloy becomes even more obvious in the mass spectra of in situ deuterated alloys. The observed stability properties reflect the different behavior of the Fe- and Co-system regarding hydrogenation and disproportionation during the HDDR process and confirm the results obtained by XPS analysis of $Nd_2(Fe_{1-x}Co_x)_{14}B$. The XPS spectra [1] indicated a more polarized Nd–Co bonding in comparison to Nd–Fe by chemical shift analysis. Both XPS and SIMS data explain on the one hand the high affinity of $Nd_2Fe_{14}B$ to hydrogen and the higher tendency for disproportionation when heat treated in hydrogen atmosphere and on the other hand the higher stability of Co containing alloys against disproportionation.

The XPS results suggested the crucial role of the lanthanoid Nd for hydrogen binding in the alloy. They reveal changes in surface composition of hydrogen-free alloys with various Co content as well as an additional hydrogen-induced change in surface composition in $Nd_2Fe_{14}B$, whereas $Nd_2Co_{14}B$ remains nearly unaffected. A surface near Nd enrichment region which is even more pronounced after hydrogenation is found in depth profiles of Fe-rich alloys. In Co-rich alloys this region is largely absent. Positive SIMS spectra of deuterated and deuterium-free alloys reveal a remarkable difference in the secondary ion emission intensity of Nd^+ and NdO^+ in $Nd_2Fe_{14}B$ and alloys with Co content $x\geq0.5$, respectively (see Fig. 1). The surface intensity ratio $I(Nd^+)/I(NdO^+)$, which can be taken as a measure for the reduction degree of Nd,

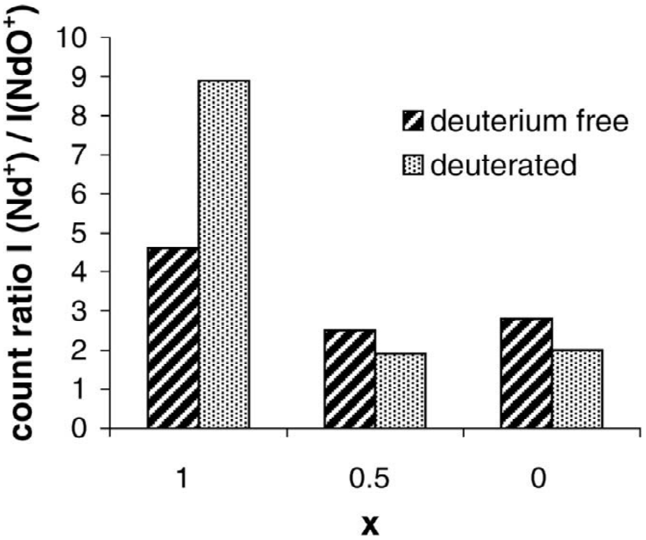

Fig. 1. Hydrogen-induced Nd-segregation/reduction in $Nd_2(Fe_xCo_{1-x})_{14}B$.

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[1] D which is normally absent in the residual gas of the analyzing chamber is used instead of H in order to be able to distinguish clearly between (more or less undefined) influences of hydrogen (H) from the atmosphere or residual gas and the hydrogen (D) in the alloy.

increases in deuterated $Nd_2Fe_{14}B$ with respect to the deuterium-free alloy by a factor 2, whereas it remains nearly unchanged in Co containing alloys. This fact is due to the presence of elementary Nd at the surface caused either by reduction by hydrogen or hydrogen-induced surface segregation of Nd. Partial substitution of Fe by Co suppresses this effect. The Nd surface segregation/reduction found by SIMS only in $Nd_2Fe_{14}B$ corresponds well to the XPS results. It indicates the major role of elementary Nd in hydrogen surface binding.

Fig. 2 shows the relative emission intensity of NdD_2^- cluster. The Me_2^- emission intensity, which is significantly different for Me=Fe and Me=Co in deuterated alloys, is chosen as a reference. The occurrence of negative deuterium cluster ions containing the electropositive lanthanoid Nd is remarkable. In that respect differences can be observed for the Fe and Co system, the standardized emission intensity of NdD_2^- decreases systematically with increasing Co content of the alloy. Although the overall hydrogen content in $Nd_2Co_{14}B$ should be lower than in $Nd_2Fe_{14}B$ after hydrogenation in an external hydrogenation chamber [2], during SIMS surface analysis applying in situ deuterium implantation no significant intensity differences of deuterium containing secondary ion cluster can be observed for the two alloys except for NdD_2^-. This trend parallels the disappearance of a surface near Nd enrichment with partial substitution of Fe by Co found by XPS [1]. It reflects the tendency of $Nd_2Fe_{14}B$ to disproportionate into NdH_2, Fe and Fe_2B. The high affinity of Nd to form NdD_2^- cluster ions is also found in SIM spectra of pure Nd. This means that the Fe alloy $Nd_2Fe_{14}B$ shows characteristic properties of the isolated elements, whereas $Nd_2Co_{14}B$ involves a strong chemical bond between Nd and Co resulting in a partial loss of emission properties of the isolated elements.

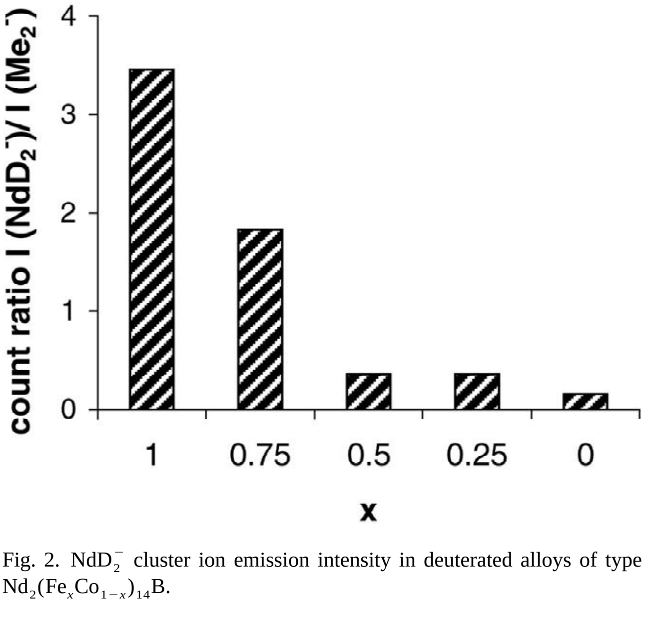

Fig. 2. NdD_2^- cluster ion emission intensity in deuterated alloys of type $Nd_2(Fe_xCo_{1-x})_{14}B$.

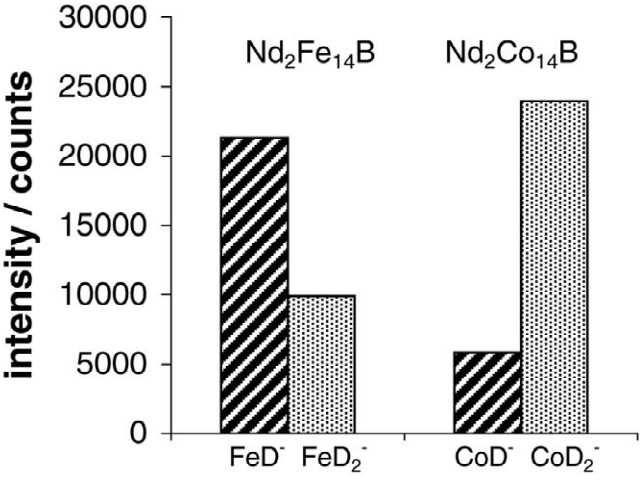

Fig. 3. Emission intensity of MeD_y^- cluster ions in $Nd_2Fe_{14}B$ and $Nd_2Co_{14}B$.

The role of the 3d transition metals Fe and Co during the hydrogenation process of $Nd_2(Fe/Co)_{14}B$ alloys is revealed by comparison of the emission of the negative cluster ions MeD^- and MeD_2^- (see Fig. 3). Hydrogen dissociation is the initial step for hydrogen uptake into interstitial sites of the alloy. The ratio $I(MeD^-)/I(MeD_2^-)$ for Me=Fe, Co can be taken as a measure for the degree of hydrogen dissociation ability. Accordingly Fig. 3 indicates that Fe is obviously better catalyst than Co. In XPS experiments [1] an Fe enrichment at the outermost surface of $Nd_2Fe_{14}B$ was found. The amount of this enrichment increases upon hydrogenation. Both SIMS and XPS data therefore suggest the crucial role of surface Fe as a catalyst for hydrogen dissociation. In Co-rich alloys no Co surface enrichment is found. The absence of the catalyst in Co-rich alloys explains the higher hydrogenation temperatures and slower hydrogen uptake kinetics of the Co alloys.

4. Summary and conclusion

The SIMS investigations provide information on the hydrogenation and thermal disproportionation behavior of $Nd_2Fe_{14}B$ and $Nd_2Co_{14}B$ alloys. The characteristic interaction of the alloy components with hydrogen and their function during hydrogenation could be analyzed and successfully interpreted following the HDDR behavior and in good agreement with previous XPS results.

The secondary ion emission pattern in deuterated and deuterium-free alloys $Nd_2(Fe_{1-x}Co_x)_{14}B$ reflects the stabilizing effect of Co and a hydrogen-induced disproportionation tendency of Fe-rich alloys into the isolated components. Hydrogen-induced Nd surface segregation/reduction suggests the crucial role of the electropositive lanthanoid for the hydrogenation process. The formation of negative NdD_2^- cluster ions corresponds to the high affinity of deuterium to Nd. The affinity decreases significantly with rising Co content of the alloy showing that electronic effects are remarkably involved in the hydrogen binding process.

Both the high affinity of deuterium to Nd and the different catalytic activity of the transition metal for hydrogen dissociation measured by the ratio $I(\mathrm{MeD}^-)/I(\mathrm{MeD}_2^-)$ explain the different thermal hydrogenation and disproportionation behavior of the Fe and Co-alloy during the HDDR process.

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