

Interaction of Hydrogen with the Intermetallic Compounds Sc₂Al and Sc₂Ni

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Abstract—The reactions of the intermetallic compounds Sc₂Al and Sc₂Ni with hydrogen have been investigated. The results demonstrate that Sc₂Ni reacts with hydrogen even at room temperature, to form amorphous Sc₂NiH₅. The reaction is irreversible at room temperature. Vacuum extraction of hydrogen between room temperature and 900°C leads to partial decomposition of Sc₂NiH₅ and the formation of crystalline ScH₂ and ScNi₂. Sc₂Al is nonreactive with hydrogen at room temperature. Heating at a hydrogen pressure of 5 MPa leads to Sc₂Al hydrogenolysis starting at 225°C and the formation of ScH₂ and metallic Al.

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INTRODUCTION

Among the fundamental issues in hydrogen energy development, the creation of novel hydrogen storage and transport materials with tailored sorption characteristics and dissociation pressures of their hydrides is of particular importance. At the same time, there are many intermetallic compounds with unique properties which have not yet found practical application on a proper scale. Among such compounds are rare-earth-rich intermetallics, such as R₃M and R₂M (R = rare-earth element, M = transition metal), which may be of practical interest and are potentially attractive as model systems for gaining insight into the fundamental aspects of the chemistry of hydrides. Convincing evidence of equilibrium interaction between such intermetallics and hydrogen is, however, still lacking. This issue was addressed earlier in several reports [1–8]. The interesting, though somewhat contradictory, results of previous studies led us to focus on this family of rare-earth-rich compounds. The scandium compounds of this family, in particular Sc₂Al and Sc₂Ni, have been studied very little. In this paper, we report our findings on the interaction of Sc₂Al and Sc₂Ni with hydrogen.

EXPERIMENTAL

Sc₂Al and Sc₂Ni were synthesized from high-purity metals: 99.956% Sc (bisublimed), 99.99% Al, and 99.99% Ni. Commercial scandium was purified by vacuum sublimation in a graphite-heater furnace at a residual pressure of $1.33 \times (10^{-3} - 10^{-4})$ Pa [9].

The starting mixture was arc-melted in a water cooled copper hearth using a nonconsumable tungsten electrode under a high-purity helium atmosphere at a pressure of $\approx 10^5$ Pa. The samples were remelted three or four times to improve the chemical homogeneity of the alloys. Interaction of Sc₂Al and Sc₂Ni with hydrogen was studied using a purpose-designed hydrogenation apparatus at pressures from 0.001 to 10 MPa and also by high-temperature vacuum extraction in the range 25–900°C. The hydrogen content of hydrides was evaluated using a modified van der Waals equation.

The intermetallics and hydrides were characterized by x-ray diffraction (XRD) on a DRON-2 powder diffractometer (CuK α radiation, silicon standard). In data processing, we used RIETAN-200 software. The samples were ground in an agate mortar, and the resultant powders were placed in a quartz holder and secured with x-ray amorphous film. All manipulations were performed in a nitrogen-filled box.

RESULTS AND DISCUSSION

Structural characterization of Sc₂Al and Sc₂Ni.

As shown by XRD examination, Sc₂Al has the Ni₂In (*hP6*) structure with lattice parameters $a = 4.88$ Å and $c = 6.166$ Å, and Sc₂Ni has the Ti₂Ni structure (sp. gr. *Fm3d*) with $a = 11.318$ Å. The indexing results agree well with earlier data [10] and demonstrate that both compounds were essentially phase-pure.

Interaction of Sc₂Al with hydrogen. Attempts to hydride Sc₂Al at room temperature were unsuccessful:

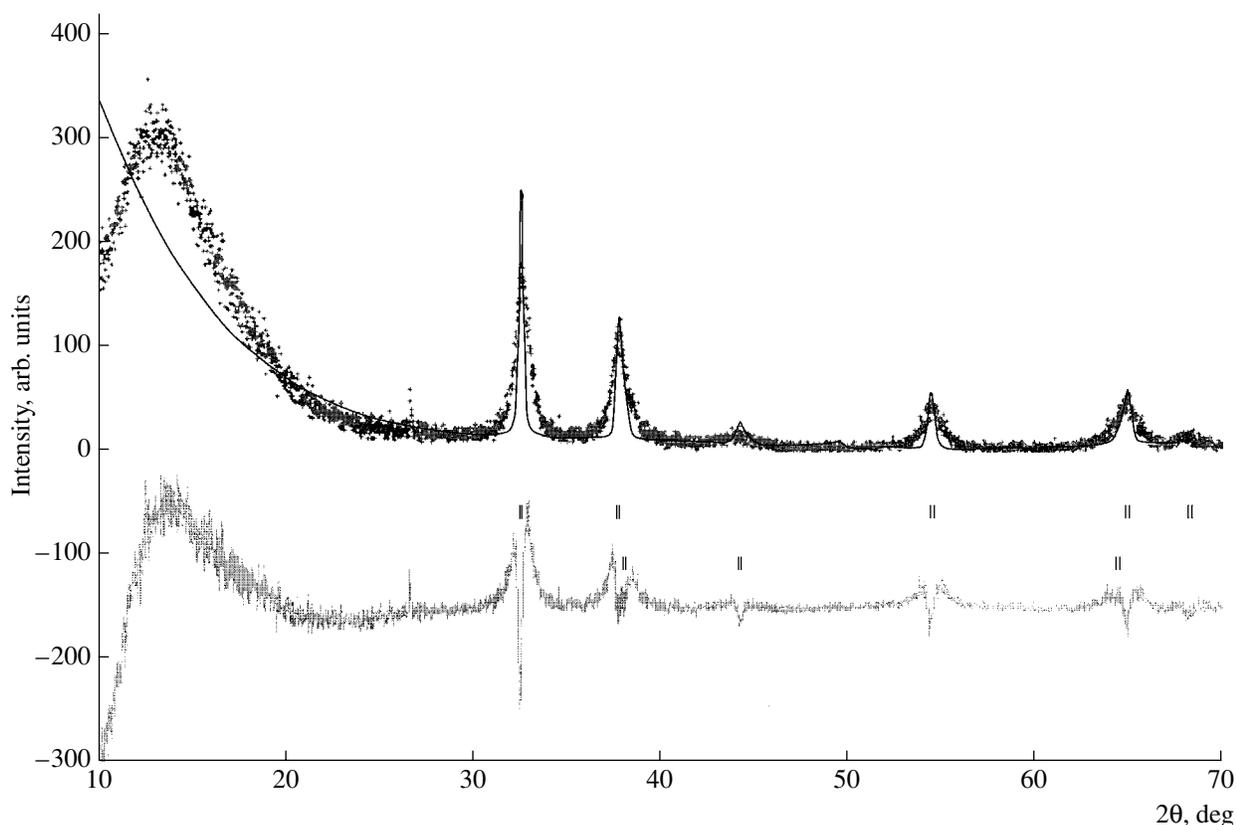


Fig. 1. XRD pattern of the decomposition products of hydrided Sc_2Al ; the upper and lower tick marks show the positions of reflections from ScH_2 and Al, respectively.

in the pressure range 5–7 MPa, no reaction with hydrogen was detected. During slow heating at a hydrogen pressure of 5 MPa, reaction began at 225°C. The amount of absorbed hydrogen was 4.0 hydrogen atoms per formula unit ($\text{H} : \text{Sc}_2\text{Al} = 4$). The XRD pattern of the resultant compound is displayed in Fig. 1.

As is well known [1, 2], the reaction between hydrogen and an intermetallic compound may follow different paths, leading to drastically different reaction products. The most likely reaction mechanism is hydrogenolysis, resulting in complete decomposition of the compound and the formation of a stable AH_x hydride and an A_mB_n intermetallic compound (enriched in the metal nonreactive with hydrogen) or B metal. Being the most thermodynamically favorable process, hydrogenolysis is the least interesting for practical application. To ascertain which process—the formation of a single-phase intermetallic hydride or hydrogenolysis—is more likely, one should compare the enthalpies of formation of the parent intermetallic compound and expected hydriding products. In particular, a relatively low heat of formation of a rare-earth intermetallic compound in combination with a relatively high heat of formation of its hydride favors the hydrogenolysis process.

The heat of formation of scandium dihydride is rather high, 50 kcal/mol [11], whereas that of Sc_2Al is about 7 kcal/mol [12]. It seems, therefore, likely that, under the conditions of this study, the hydriding of Sc_2Al occurs according to the scheme

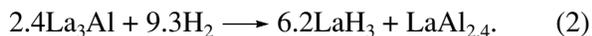


i.e., follows the most thermodynamically favorable mechanism—hydrogenolysis.

This is supported indirectly by the fact that an attempt to isothermally decompose the synthesized hydride was unsuccessful: reducing the pressure from 5 to 0.01 MPa caused no hydrogen release. This may be interpreted as evidence for the formation of the very stable compound ScH_2 , whose decomposition temperature exceeds 1200°C and was not attained in our experiments.

Analysis of phase transformations in R–Al–H systems [4, 5] shows that the R_3Al , R_2Al , R_3Al_2 , and RAl ($\text{R} = \text{Y}, \text{Sc}, \text{La}, \text{Ce}, \text{Pr}, \text{Ho}, \text{Er}$) intermetallics are to some extent subject to hydrogenolysis or do not react with hydrogen at all. La_3Al reacts with hydrogen most

readily, experiencing hydrogenolysis according to the scheme



The mechanism underlying the interaction of these compounds with hydrogen was analyzed by Semenenko et al. [5], who studied the reactions of R_xAl_y ($\text{R} = \text{Ce}, \text{Pr}, \text{Ho}, \text{Er}, \text{Sc}, \text{Y}$) intermetallics with hydrogen in broad temperature and pressure ranges by XRD and differential thermal analysis. Their results demonstrate that, at 573 K, hydrogenolysis leads to the formation of rare-earth hydrides and aluminum-enriched intermetallics or rare-earth hydrides and Al metal. The phases forming at 300 K and lower temperatures are x-ray amorphous superstoichiometric hydrides and crystalline hydrogenolysis products.

In light of this, it is reasonable to assume that the hydriding of Sc_2Al occurred according to scheme (1), i.e., by the hydrogenolysis mechanism, leading to the formation of the stable hydride ScH_2 . This is also supported by the amount of absorbed hydrogen, $\text{H} : \text{Sc}_2\text{Al} \approx 4$, which corresponds to the stoichiometry of reaction (1). Direct evidence of this reaction path is provided by the XRD results for the hydriding products (Fig. 1): all of the observed diffraction peaks correspond to scandium dihydride (sp. gr. $Fm\bar{3}m$, $a = 4.775 \text{ \AA}$) and aluminum (sp. gr. $Fm\bar{3}m$, $a = 4.038 \text{ \AA}$). In addition, the diffraction line profiles point to partial amorphization of the hydriding products.

The present results, as well as some of the earlier data, are in conflict with the report by Antonova and Chernogorenko [3] that, after repeated hydriding–dehydriding cycles, the sorption capacity of Sc_2Al for hydrogen is $\text{H} : \text{Sc}_2\text{Al} = 4$. They described a reversible hydriding process and thermally stable hydrides which might be used as hydrogen storage materials. Their conclusions, however, appear highly questionable because neither the starting alloys nor the hydriding products in that study were characterized by XRD.

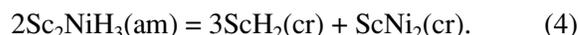
Interaction of Sc_2Ni with hydrogen. Sc_2Ni was hydrided at room temperature at 5 MPa using the same hydrogenation apparatus. A characteristic feature of the hydriding process in this system is a long induction period (several hours). The amount of absorbed hydrogen was $\text{H} : \text{Sc}_2\text{Ni} = 5.0$. An attempt to isothermally decompose the synthesized hydride was unsuccessful, which attests to a very low equilibrium pressure in the system Sc_2Ni hydriding products–hydrogen, i.e., to stability of the hydride.

According to XRD data, the hydriding of Sc_2Ni led to the formation of an x-ray amorphous compound or a mixture whose composition can be evaluated from earlier data on the hydriding of rare-earth-rich compounds with Al [2, 4, 5] and R_3Ni compounds [7, 8].

The hydriding of such compounds under mild conditions leads to the formation of x-ray amorphous hydrides which contain more hydrogen than do the products of hydrogenolysis under severe conditions. Calculations indicate that the amount of hydrogen absorbed by Sc_2Ni during hydriding exceeds that needed for the reaction under more severe conditions, which would be accompanied by hydrogenolysis and the formation of a rare-earth hydride and, possibly, Ni or an Sc–Ni alloy. This gives grounds to assume that the x-ray amorphous phase is a hydride of the parent intermetallic compound:



The properties of the x-ray amorphous hydride were studied by two-step vacuum extraction of hydrogen. The purpose of the first step was to determine the onset temperature of hydrogen release. The sample was heated from room temperature to 310°C , where hydrogen release began. XRD examination showed that, after heating to 310°C , the sample remained amorphous. In the second step of vacuum extraction, we examined the possibility of hydrogen desorption during heating from 310 to 900°C . Hydrogen release was only observed in the range $310\text{--}350^\circ\text{C}$, and the amount of desorbed hydrogen corresponded to $\text{H} : \text{Sc}_2\text{Ni} = 2$. Heating the sample from 350 to 900°C produced no changes in this ratio. The relationship between the amount of hydrogen released as a result of vacuum extraction and that absorbed during hydriding by reaction (3) provides indirect evidence that, during heating, amorphous Sc_2NiH_5 decomposes to form crystalline hydrogenolysis products, one of which is, as usually, a dihydride: Sc_2Ni . The hydrogen content of scandium dihydride corresponds to the amount of hydrogen that was not desorbed during heating from 350 to 900°C , since, as mentioned above, the decomposition temperature of scandium hydrides exceeds 1200°C :



The above assumptions based on high-temperature vacuum extraction results were confirmed by XRD examination of the sample after vacuum extraction of hydrogen in the temperature range $300\text{--}900^\circ\text{C}$ (Fig. 2). As expected, high-temperature heat treatment was shown to result in the decomposition of amorphous Sc_2NiH_5 and subsequent crystallization of the hydrogenolysis products: all of the observed diffraction peaks corresponded to scandium dihydride (sp. gr. $Fm\bar{3}m$, $a = 4.775 \text{ \AA}$) and ScNi_2 (sp. gr. $Fd\bar{3}m$, $a = 6.923 \text{ \AA}$).

Note that Semenova et al. [6] investigated the reactions of the Sc_2Ni , ScNi , ScNi_2 , Sc_2Ni_7 , and ScNi_5 intermetallics with hydrogen in the temperature range $20\text{--}900^\circ\text{C}$ at a hydrogen pressure of 0.3 MPa. The maximum absorption capacity was determined to be 3.42, 3.04, 1.84, 3.2, and 1.71 wt %, respectively, which cor-

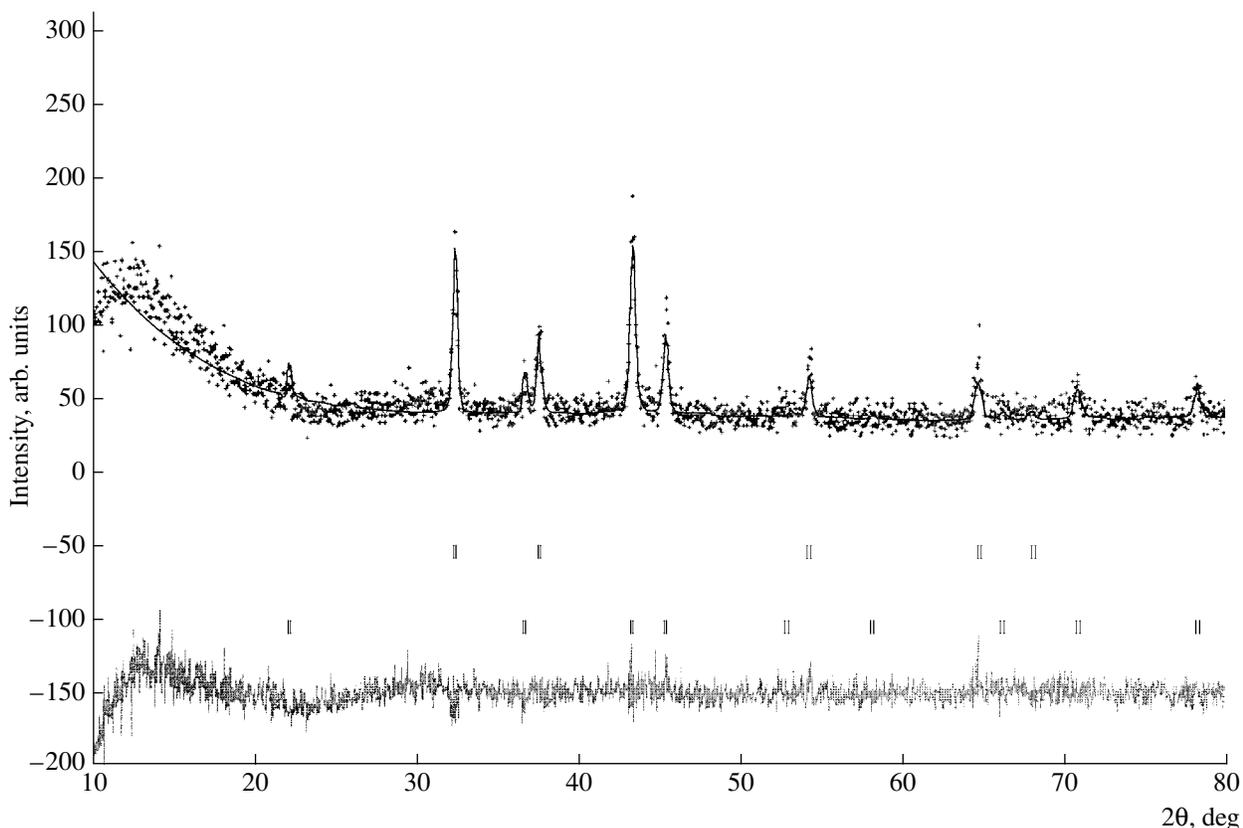


Fig. 2. XRD pattern of the decomposition products of amorphous Sc_2NiH_5 after vacuum extraction of hydrogen in the temperature range 300–900°C; the upper and lower tick marks show the positions of reflections from ScH_2 and ScNi_2 , respectively.

responds to the stoichiometries $\text{Sc}_2\text{NiH}_{4.6}$, $\text{ScNiH}_{3.65}$, $\text{ScNi}_2\text{H}_{3.02}$, $\text{Sc}_2\text{Ni}_7\text{H}_{1.92}$, and $\text{ScNi}_5\text{H}_{8.7}$. All of these hydrides were reported to be thermally stable, with the lowest decomposition temperature of 200°C ($\text{ScNiH}_{3.65}$), but the decomposition of this hydride did not reach completion even at 400°C. Since Semenova et al. [6] presented no XRD data, comparison with our results is impossible.

CONCLUSIONS

The present results demonstrate that, at room temperature, Sc_2Al does not react with hydrogen. Heating to 300°C leads to Sc_2Al hydrogenolysis and the formation of ScH_2 and metallic Al. The high temperature of hydrogen desorption from scandium dihydride (above 1200°C) prevents Sc_2Al from being used as a hydrogen storage material.

Sc_2Ni reacts with hydrogen even at room temperature, to form amorphous Sc_2NiH_5 . The reaction is irreversible at this temperature. The amount of hydrogen desorbed in the temperature range 310–350°C corresponds to $\text{H} : \text{Sc}_2\text{Ni} \approx 2$. Further heating leads to hydrogenolysis and crystallization of ScH_2 and ScNi_2 . The formation of the stable high-temperature compound

ScH_2 rules out the use of Sc_2Ni as a hydrogen storage material.

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