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Effect of Hydrogen Absorption-Desorption Cycle on the Magnetic Susceptibility of $CeNi_4Al$*

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The effect of hydrogen on the magnetic susceptibility of $CeNi_4Al$ has been investigated. It is observed that following a hydrogen absorption–desorption cycle, without exposing the sample to air, the magnetic susceptibility of $CeNi_4AlH_0$(I) increases over that of $CeNi_4Al$. If, after hydrogenation, the sample is kept in the air and then hydrogen removed, the increase in susceptibility of $CeNi_4AlH_0$(II) is even larger. Magnetic precipitation of Ni due to the presence of O_2 and H_2O is thought to be responsible for this behavior. An increase in susceptibility of $CeNi_4AlH_{3.7}$ over that of $CeNi_4Al$ is also observed and attributed partly to the tendency of valence change of cerium from 4+ toward 3+.

Introduction

A number of alloys and intermetallic compounds are capable of absorbing large quantities of hydrogen (for a review of this field, see Ref. (*1*)). In recent years, these metal–hydrogen systems have attracted considerable attention because of their possible use as hydrogen storage materials for energy-related applications since hydrogen is being projected as a future energy source. One of the more promising materials for such applications is $LaNi_5$. At ambient temperatures and pressures, this compound absorbs hydrogen to form $LaNi_5H_{6.7}$ which has a proton density of $6.2 \times 10^{22}/cm^3$—about 50% larger than that of liquid hydrogen. Further, the ease with which hydrogen is absorbed and desorbed by $LaNi_5$ is remarkable (*2*).

In a recent communication from this laboratory hydrogen absorption characteristics of a series of compounds of the general formula RNi_4Al (R = rare earth) were reported (*3*). These compounds are isostructural with the RNi_5 compounds from which they are derived by substitution of one Ni by one Al atom. In both series of compounds the original crystal structure, as determined by X-ray diffraction, is maintained (for a review of this field, see Ref. (*1*)) on hydrogen absorption. Incorporation of hydrogen in the lattice merely results in an expansion of the lattice. On Al substitution the amount of hydrogen absorbed sharply decreases. For example, $LaNi_4AlH_{4.3}$ is formed in place of $LaNi_5H_{6.7}$. However, Al substitution increases the stability of corresponding hydride in the sense that plateau pressures of the $RNi_4Al–H_2$ systems are lower than

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those of the RNi$_5$–H_2 systems. The decrease is by several orders of magnitude in some systems.

One problem in using rare earth intermetallic compounds as hydrogen storage materials is that they may become modified and degraded as a result of repeated hydrogen absorption–desorption cycles. It is well known that LaNi$_5$ is modified by cycling in that La is oxidized and elemental nickel forms (*4*). This transformation is without effect for up to 1000 cycles (R. F. Karlicek, Jr., unpublished measurements) but at some large limit all the LaNi$_5$ would be converted and the material would cease to function as a storage material. We have performed magnetic susceptibility measurements on one member of the RNi$_4$Al series, namely, CeNi$_4$Al, to ascertain whether there is precipitation of Ni during cycles of absorption–desorption of hydrogen similar to those observed for LaNi$_5$ ((*4*); R. F. Karlicek, Jr., unpublished measurements). The choice of the Ce compound rather than the conventional La compound involved other considerations as well—the possible change in the valence state of cerium on hydrogen absorption (see below). We find, as is indicated in detail below, that CeNi$_4$Al shows degradation effects, probably due to the formation of Ni on the sample surface (due to the presence of O_2 and H_2O) during hydrogen absorption–desorption cycles. This is also likely to be the case in other RNi$_4$Al compounds.

Experimental

The compound CeNi$_4$Al was freshly prepared for the present experiment. The purity of the starting materials, the method of preparation of the intermetallic compound, and the structural analysis by powder X-ray diffraction patterns have been described in the earlier paper (see Ref. (*3*)). The magnetic susceptibility measurements were carried out using the Faraday method over the temperature range 4.2 to 300 K and in an applied field of 21 kOe. Hydrogenation was carried out in a system of fixed volume. Prior to hydrogenation, the sample was degassed by heating it to 150°C while continuously pumping. Hydrogen was introduced after cooling the sample to room temperature. All the samples on which results of susceptibility measurements are described below were taken from the same ingot of CeNi$_4$Al which had been well homogenized by repeated melting so as to avoid any changes due to stoichiometry fluctuation.

Results and Discussion

The sample of CeNi$_4$Al which was processed through one absorption–desorption cycle without exposure to air after hydrogenation is termed CeNi$_4$AlH$_0$(I). The sample termed CeNi$_4$AlH$_0$(II) was obtained by following another procedure (see below). Figure 1 shows the temperature variation of the magnetic susceptibility of CeNi$_4$Al, CeNi$_4$AlH$_0$(I), and CeNi$_4$AlH$_0$(II), none of which contains any hydrogen. The susceptibility of CeNi$_4$Al is the smallest of the three and almost temperature independent. The observed susceptibility behavior is a consequence of Ni being nonmagnetic in the RNi$_4$Al compound, as in the RNi$_5$ compound and, in addition, cerium being present in the 4+ state. On one absorption–desorption cycle the susceptibility of CeNi$_4$(AlH$_0$(I) has increased appreciably compared with that of virgin CeNi$_4$Al. This suggests the formation or precipitation of a magnetic phase or constituent, most likely Ni metal during this process. The powder X-ray diffraction pattern of CeNi$_4$AlH$_0$(I), however, did not show the presence of Ni or another phase and was identical with that of CeNi$_4$Al.

To further investigate the magnetic pre-

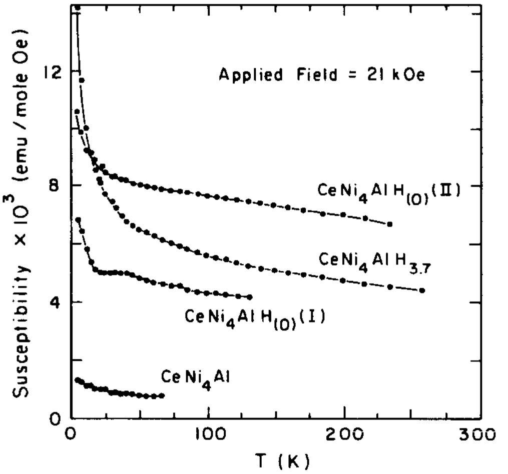

FIG. 1. Plot of magnetic susceptibility versus temperature for $CeNi_4Al$, $CeNi_4AlH_0$(I), $CeNi_4AlH_0$(II), and $CeNi_4AlH_{3.7}$. For explanation of terminology, see text.

cipitation we prepared another sample termed $CeNi_4AlH_0$(II) by the following procedure. A part of $CeNi_4Al$ was fully hydrogenated to $CeNi_4AlH_{3.7}$. It was kept in air for a few hours, then transferred back to the hydrogenation cell and the hydrogen removed by heating the sample while continuously pumping. The powder X-ray diffraction pattern of $CeNi_4AlH_0$(II) was again devoid of any extraneous phases (within the sensitivity of the X-ray method) and was identical with those of $CeNi_4Al$ and $CeNi_4AlH_0$(I); its susceptibility, however, is even larger compared to that of the other two. The increase in susceptibility is presumed to arise from the fact that during exposure to air, the sample picks up oxygen and water molecules which later react with the sample and precipitate Ni when the sample is heated to desorb hydrogen. In the case of $CeNi_4AlH_0$(I), which is exposed to air only after the completion of the absorption–desorption cycle, the precipitation of Ni is caused by the traces of impurity—oxygen, etc.—which are present either in the hydrogenation cell or in the intermetallic compound. A similar behavior has also been observed (*4*) in $LaNi_5$ and is expected (*5*) generally for rare earth intermetallic compounds.

In Fig. 1 we also present the temperature variation of magnetic susceptibility of $CeNi_4AlH_{3.7}$. An increase in susceptibility of this compound on hydrogenation is noted. From a comparison of the lattice parameters of RNi_4AlH_x with those of RNi_4Al it had been suggested earlier (*3*) that on hydrogen absorption Ce in $CeNi_4Al$ may have changed its valence state from 4+ to some intermediate value tending toward 3+. Such a valence change in the case of cerium is not unlikely since it is known that application of pressures can bring about Ce^{3+} to Ce^{4+} change (*6*). Introduction of hydrogen in rare earth intermetallics leads to an expansion of the lattice and is in some respects equivalent to a negative pressure so that an inverse transition from Ce^{4+} toward Ce^{3+} is very likely. Of course, addition of hydrogen is not the identical equivalent of a negative pressure because hydrogen also introduces electrons and electronic states which interact and admix with those already existing in the host material. Thus lattice parameter considerations and the observation of the increase in susceptibility, and particularly the enhanced temperature coefficient of susceptibility, of $CeNi_4AlH_{3.7}$ over those of $CeNi_4Al$ and $CeNi_4AlH_0$(I), give suggestive evidence of a valence change of cerium from Ce^{4+} toward Ce^{3+}. Of course, part of the increase in susceptibility is due to the precipitation of Ni caused by the traces of O_2 and H_2O which are present during the hydrogenation process and in this respect $CeNi_4Al$ behaves in a manner similar to that of $LaNi_5$.

Further evidence for the precipitation of a ferromagnetic substance comes from the results of magnetization versus applied field at 4.2 K, shown in Fig. 2. The magnetization of both $CeNi_4AlH_0$(I) and (II) indicates a component which tends to saturate relatively easily. The field dependence is char-

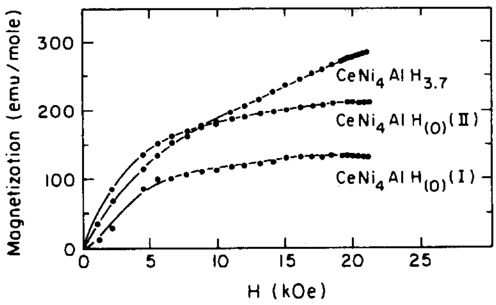

FIG. 2. Magnetization versus applied field at 4.2 K.

acteristic of a mixture of ferromagnetic and superparamagnetic elemental nickel. Thus the data for these materials suggest that they contain significant amounts of precipitated nickel. The magnetization-field curve for $CeNi_4AlH_{3.7}$ is different; it does not show saturation at the fields employed. Its magnetization appears to be dominated by the proportion of Ce^{3+} in the sample. The curvature at low fields is ascribed to Ni precipitation, the quantity being less than that of the two dehydrogenated samples. This suggests that dehydrogenation is more important for the nickel precipitation than the hydrogenation portion of the cycle.

The susceptibility computed from the linear portion of the curve for $CeNi_4AlH_{3.7}$ in Fig. 2 can be used to compute a fraction of Ce which is converted into the tripositive state by hydrogenation. This is found to be 4.6 mole%. Assuming the correctness of this calculation, we would conclude that the Ce^{4+}/Ce^{3+} system is too magnetically dilute to exhibit magnetic ordering effects and instead behaves as a dilute assemblage of uncoupled tripositive magnetic ions.

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