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Final Report

Phase I. Lanthanum-based Start Materials for Hydride Batteries

by

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The sum of the work performed under this CRADA is potentially patentable.
This final report contains non-proprietary results suitable for public dissemination

The purpose of Phase I of this work is to focus on developing a La-based start material for making nickel-metal (lanthanum)-hydride batteries based on our carbothermic-silicon process. The goal is to develop a protocol for the manufacture of $(La_{1-x}R_x)(Ni_{1-y}M_y)(Si_z)$, where R is a rare earth metal and M is a non-rare earth metal, to be utilized as the negative electrode in nickel-metal hydride (NiMH) rechargeable batteries.

Carbothermic reactions are thermochemical reactions which use carbon as the reducing agent at a high temperature to prepare the metals and alloys of interest. The most prominent example is used in iron ore smelting. Over the last 100 years various attempts have been made to prepare refractory and rare earth metals and alloys by carbothermic processing. Some success was achieved, but high purity materials were not obtained and consistently contained large amounts of carbon (usually as metallic carbides) and other interstitials, including unreacted oxides.

At the Ames Laboratory, in the 1950's and early 1960's, H.A. Wilhelm and associates developed processes for preparing high quality (purities of 99% plus) niobium metal and vanadium metal by the carbothermic process. The advent of electron beam melting greatly contributed to these processes and allowed the completion of the elements in pure form.

In 2005 we developed the carbothermic reduction method for preparing the magnetic refrigerant alloys $Gd_5(Si_xGe_{1-x})_4$ which had magnetocaloric properties equal to or better than those prepared from commercial materials. Additional studies were made in which rare earth metals were carbothermically reduced in the presence of an alloying agent to form a master alloy to be used in further processing. In 2008 we prepared a Nd_5Si_3 master alloy that was used to produce $Nd_2Fe_{14}B(Si)$ bonded magnets. Patents covering both of these processes were filed in 2010. The carbothermic process for preparing rare earth alloys is fast, efficient, low cost and has green technology since the alloy of interest can be prepared in a single heating step. The reaction proceeds by the equation,

$$R_2O_3+M_yO+C \xrightarrow[vac]{\Delta} RM_y+CO(g)$$

The by-product gas CO can be used as a heating source, and no slags are produced that require disposal.

During the course of the CRADA, which began in February 1, 2011 and ended on March 31, 2013, we were successful in developing the carbothermic reduction process to prepare $R(Ni_{1-x}Co_x)_{4.5}Si_{0.5}$ alloys for use in NiMH rechargeable batteries. The rare earth (R) oxide is either: (1) directly reduced with carbon in the presence of silicon to form a $R\text{-}Si_{0.5}$ master alloy which is added to nickel and/or cobalt; or (2) the R oxide is reduced with carbon in the presence of nickel and/or cobalt without additions of silicon to form the $R(Ni_{1-x}Co_x)_5$ alloy.

In our first studies, standard $LaNi_{4.5}Si_{0.5}$ and $LaNi_5$ alloys were prepared from commercial material by arc-melting and drop-casting. These alloys had a hydrogen storage capacity of 3.9 max H/f.u. for the $LaNi_{4.5}Si_{0.5}$ alloy and 6.0 max H/f.u. for the $LaNi_5$ alloy.

The carbothermic process was used to prepare several $RSi_{0.5}$ alloys which could be alloyed with nickel for $RNiSi_{0.5}$ electrode materials. Also, a single-step process was developed for preparing RNi_5 alloys from which metal hydride alloys having good hydrogen storage capacities were prepared and alloys of improved quality should be possible with additional studies.

A patent disclosure covering this work has been drafted and will be submitted in the near future.

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