WSRC-TR-92-594

DEVELOPMENT OF METAL HYDRIDE COMPOSITES (U)

by
J. W. Congdon

Savannah River Site
Aiken, South Carolina 29808

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J. W. Congdon

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Westinghouse Savannah River Company
P. O. Box 616
Aiken, SC 29802

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APPROVALS

J.W. Congdon Date: 12-21-92

J. W. Congdon, Author
Materials Compatibility & Joining Technology Group
Materials Technology Section

James C. Marra Date: 12-21-92

J. C. Marra, Technical Reviewer
Materials Technology Section

D. T. Rankin Date: 12/21/92

D. T. Rankin, Manager
Materials Compatibility & Joining Technology Group
Materials Technology Section

Date: 12/21/92

T. L. Capeletti, Manager
Materials Technology Section

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EXECUTIVE SUMMARY

Most of the current hydride technology at the Savannah River Site (SRS) is based on the use of beds of metal hydride powders. A large expansion occurs when the hydride forms and cycling results in the continued breakdown of the powders into finer particles. The goal of this program is to eliminate the detrimental effects of the expansion of the metal hydride and of the fine particles by developing a composite which will contain the fines in a dimensionally stable matrix. The development of a stable composite is particularly important in processes which require a stable gas flow through a hydride bed.

Metal hydride composites would benefit the advanced Thermal Cycling Absorption Process (TCAP) by improving the efficiency of the hydrogen isotope separation process. Composites would provide advantages throughout the Replacement Tritium Facility (RTF) for the storage, pumping, compression, and purification of hydrogen isotopes. Commercial applications for metal hydride composites are also feasible.

The results of this study have demonstrated that a dimensionally stable metal hydride composite can be formed by using pore formers to create sufficient porosity around the metal hydride to accommodate the expansion and minimize the stress in the matrix. These composites were fabricated by the cold compaction of a mixture of metal hydride granules and coarse copper powder. The porosity in the metal granules was introduced by using ammonium carbonate as a pore former. The ammonium carbonate decomposed in air at room temperature without affecting the ability of the metal hydride to store hydrogen.

Cyclic absorption/desorption testing in hydrogen indicates that the hydrogen storage capacity and the hydrogen absorption/desorption rates are satisfactory. The matrix remained integral and uncracked after cyclic absorption/desorption tests. As expected, metal hydrides on the surface of the composite were lost after only a few cycles. This eventually resulted in a pitted surface with occasional degradation of the edges. These tests were all performed on unsintered copper matrix composites.

Development work will continue to minimize the loss of hydrides from the surface and the mechanical degradation of the edges of the

pellets. The current program to develop a microporous or hydrogen permeable coating also will continue. The optimum processing conditions and the process limits will be determined. Additional testing is also needed to evaluate the separation efficiency of the composite and to expose the composite pellets to more severe testing conditions. The composites will also be exposed to tritium to evaluate the effects of the decay helium on the performance of the composite. The fabrication process must be scaled-up for production utilizing automatic granulators and presses.

INTRODUCTION

Most elemental metals and many metal alloys are capable of reacting with hydrogen to form a hydride. The reaction is reversible at moderate temperatures and pressures. These materials can be utilized to rapidly absorb and desorb hydrogen and hydrogen isotopes. Metal hydrides will be used in the Replacement Tritium Facility (RTF) to pump, store, compress, purify, and separate hydrogen isotopes.

As metal alloys absorb hydrogen to form a metal hydride, the material expands and begins to fracture and break apart into smaller pieces. Continued hydrogen desorption and absorption cycles eventually result in the creation of some submicron particles. The early stages of this decrepitation process have been studied by Mosley.[1]

The expansion which occurs when a metal hydride forms has the potential to stress the container. As the material breaks down, properties which are dependent upon the surface area are affected. The rate of hydrogen absorption and desorption, as well as the heat transfer characteristics of the material, are altered. Filters are required to contain the fine particles. If fine metal hydride particles migrate past the filters, the abrasive particles are likely to degrade the performance of the valves in the system. The gas flow rates through the powder beds decrease as the particle size decreases.

For most of the metal hydride applications in the RTF, the hydride beds and filtering systems have been designed to minimize the detrimental effects of the fines which are generated after repeated cycling. However, a more stable form of the metal hydride will be required for future applications such as the advanced Thermal Cycling Absorption Process (TCAP). The gas flow through beds of fine powder is not acceptable for this separations process. The replacement of the TCAP plug flow reverser column with a column containing a dimensionally stable form of metal hydride which preferentially absorbs tritium would allow stackable deuterium (<5 ppm tritium) to be made in the RTF. In the current process, the deuterium gas containing low levels of tritium will be transferred from the RTF to the Separations building for processing by the cryogenic distillation columns.[2]

Several different metal hydride composite systems have been evaluated. Metal hydride particles have been incorporated into matrices of aluminum using standard powder metallurgy techniques to form pellets[3], into silica and alumina based cements to form porous granules[4], and into porous silica glass formed by a sol gel process[5].

In these particulate composites, the metal hydride particulates were the discontinuous phase and were surrounded by the matrix material. The absorption of hydrogen by the metal hydride is accompanied by a large volume expansion since the density of the metal hydride is lower than the density of the metal alloy. Localized stress and microcracking in the matrix result from the formation of the metal hydride. Continued cycling results in the growth of cracks and the fracture of the composite.

Electrodes for rechargeable batteries have been fabricated by compacting copper coated metal hydride powders.[6,7] These copper matrix composites were resistant to fracture because the copper was ductile enough to yield without failure as the hydride forms. Expansions of 30 volume percent were reported for this composite. Efforts to duplicate this process at SRS were abandoned due to the escape of the metal hydride from the matrix in long term testing.

In this study, a composite design was evaluated based on the incorporation of sufficient porosity around the metal hydride to accommodate the expansion and, thereby, reducing the stresses to the matrix.[8] The process development and testing programs for this metal hydride composite are described in this report.

This study focused on the development and testing of composites containing the metal alloy $LaNi_{4.25}Al_{0.75}$ (LANA0.75). The technology described in this report could be applied in developing other metal hydride composites if the metal hydride, matrix material, and pore former are compatible. The processing studies were done using laboratory-scale equipment. Testing of the composites was limited by the number of cycles and the small amount of material involved in the tests. All of these tests were performed in pure hydrogen, rather than in the hydrogen isotopes which will be used in the RTF.

The composite development and fabrication studies were performed as per the Nuclear Reactor Technology and Scientific Computations (NRTSC) Department quality assurance requirements for scoping activities on a non-critical task.[9] The hydrogen cyclic absorption/desorption tests were performed by the Hydrogen Technology Section according to the quality assurance manual for the Defense Waste Processing & Hydrogen Technology (DWP&HT) Department[10].

The Composite Design section of this report includes the hypothesis for this development work, the design basis, and a proposal for the design of a dimensionally stable metal hydride composite. The equipment, instrumentation, and test procedures are described in the Experimental section. A synopsis of the development and testing program, including some of the unsuccessful approaches to fabricating the composite, is presented in the Results. The next section describes the process flowsheet for the fabrication of a copper matrix composite containing porous granules of LANA0.75. The brief list of the Conclusions is followed by the Future Work section which describes the additional studies which will be performed to improve the process, to optimize the process, and to complete the testing program.

COMPOSITE DESIGN

A large increase in volume is associated with the hydride formation since the density of the hydride is much lower than that of the metal or metal alloy. The formation of a metal hydride creates internal stresses which are sufficient to fracture the metal hydride. Continued cycling results in the creation of submicron particles.

For many applications it would be desirable to contain the metal hydride in a matrix material to prevent the dispersion of fines and to eliminate stresses to the container. If metal hydride particulates are dispersed in a matrix using standard processing techniques, the large volume expansion will create very high localized stresses around the particulates. Since the matrix must have sufficient continuous porosity to allow for the transfer of hydrogen, it is difficult to develop a matrix which has sufficient strength or ductility to accommodate the expansion of the metal hydride without fracturing. Continued absorption/desorption cycling of these particulate composites will result in additional cracking and the eventual loss of integrity of the composite.

One method to produce a more stable metal hydride composite involves the formation of sufficient porosity around the particulates to accommodate the expansion which occurs when the metal hydride forms. Porosity can be created and controlled by the addition of pore formers. Pore formers are simply materials which can be added during processing and removed, usually by sublimation at elevated temperatures, to form pores. In order to be effective in metal hydride composites, the porosity must be created around the metal hydride. Furthermore, the pore former and its decomposition products must not react with the metal hydride or matrix material during processing. Several methods to form porosity around the metal hydride are discussed in this report.

The matrix must have open porosity to allow for the exchange of hydrogen gas. Basically, the matrix acts as a filter to contain the fine metal hydride particles. During the development process it was also realized that the matrix porosity must be capable of venting hydrogen rapidly enough to prevent the build-up of internal pressures in the composite during the desorption process. These pressures can be large enough to crack the matrix. During the development process it was also demonstrated that the matrix could be strengthened by vacuum sintering to help alleviate this cracking.

The proposed composite design (Figure 1) consists of porous metal hydride granules as a discontinuous phase in a porous metal matrix. Since porous metal hydride granules on the surface of the pellet cannot be contained by the matrix, it is important that the porous metal hydride granules be present as a discontinuous phase. Otherwise, linking of the porous granules would lead to the eventual loss of most the metal hydride material from the interior of the composite.

The composite design could be improved by the development of microporous coatings or hydrogen permeable coatings. Ideally, these coatings will contain all of the metal hydride within the composite, including that exposed on the surface, and allow for the rapid exchange of hydrogen without allowing high internal pressures to fracture the composite. Moreover, the development of a permeable coating will allow higher metal hydride concentrations to be used in the composite. With a coating, it will be necessary to have a continuous matrix phase to provide a strong shell for the composite.

EXPERIMENTAL

Characterization The materials were characterized throughout the process. The size distribution of fine powders was measured using a laser based particle size analyzer. It was necessary to use high viscosity glycerin or glycerin/water mixtures to keep the large, high density particles in suspension. A sonic sifter with micro-sieves was used to measure the particle size distribution of coarse feed material. Granulated materials were observed under the stereo microscope.

The pellets were weighed to +/-0.001 g on an electronic balance. The pellet dimensions were measured to +/-0.0005 cm using a digital micrometer.

X-ray diffraction (XRD) was used to determine if the LANA0.75 had oxidized or separated during sintering and to confirm that a hydride had formed during testing. Minor surface reactions or oxidation could not be detected by XRD.

Polished and fracture surfaces of the composite were observed on the scanning electron microscope (SEM). Polished surfaces were also observed on the metallograph. The mounted specimens were vacuum impregnated with epoxy after rough grinding to fix the loosely bound particles in metal hydride granules.

Thermogravimetric analysis (TGA) was used to determine the rate of evaporation of the pore former from the granules.

Processing Laboratory-scale equipment was used for processing. Granulation was performed by forcing cold pressed compacts through a series of stainless steel sieves using a stainless steel roller. Blending was accomplished by gently stirring the mixtures with a stirring rod. Die charges were weighed individually on an electronic top loading balance with a readability of +/- 0.001 g. A manual hydraulic press was used to form the compacts in stainless steel die assemblies designed to close at a fixed volume. This allowed for accurate control of the density of the pellets by controlling the mass of material loaded into the die rather than by adjusting the compaction pressures. Loading and unloading rates could not be controlled precisely using the manual hydraulic press.

Sintering An electric, fiber insulated, gas sealed, laboratory furnace with a microprocessor-based controller was used in sintering. Vacuum sintering was accomplished by sealing the specimens in quartz tubes evacuated to $<10^{-5}$ torr using the vacuum system from a portable leak detector.

Cyclic Absorption/Desorption Testing The apparatus shown in Figures 2 and 3 was used to perform preliminary screening integrity tests of each type of composite. The composites could be observed with a stereomicroscope through a quartz window in a chamber in which the pressure was cycled between 65 psig hydrogen and <50 mtorr. A video system, consisting of a high resolution video camera, monitor, and video disc recorder, was used to document the surface appearance of the test specimens after each cycle. Cycling times were generally two to three hours at pressure after evacuation. Every third cycle included overnight exposure at 65 psig hydrogen. Five to ten cycles were used to make the preliminary evaluation of the composites.

The Hydrogen Technology Section performed more quantitative tests, including both short term (5 absorption/desorption cycles) and long-term (~100 cycles) tests. The short term tests evaluated the storage capacity and the absorption/desorption rates. This was necessary to confirm that the matrix had sufficient porosity for the hydrogen to be absorbed by the metal hydride. It was also necessary to ensure that the processing and sintering did not affect storage capacity of the metal hydride. Long-term tests evaluated the ability of the composite to remain integral and to retain the metal hydride in the interior of the pellets.

The HTS cyclic test apparatus was designed to perform quantitative measurements of rates and capacities. Batches of composite pellets, containing a total of ~1 gram of LANA0.75 per batch, were cycled between 150°C, 2000 torr and 25°C, 300 torr. Each cycle required approximately 30 minutes.

RESULTS

The decrepitation process, material characterization, process development and cyclic absorption/desorption test results are described in this section. Much of the development work discussed in this section was either unsuccessful or was abandoned for other more promising approaches.

Decrepitation Process The initiation of the decrepitation process was observed and recorded using the apparatus and equipment described previously. Figures 4 and 5 illustrate the fracture of an as-received chunk (~0.5 cm. dia.) of LANA0.75 as it was being converted to a hydride at ~50 psig hydrogen and 25°C. The frame numbers coincide with the number of seconds after the onset of cracking since the recording rate was one frame/second.

The fracture process was rather violent. Rather large sections, consisting of up to 20% of the size of the original chunk, completely disintegrated during the one second intervals. Several minutes after the initial decrepitation of the primary segment, chunks of the metal hydride were observed to burst or, sometimes, appeared to jump out of the field of view. These observations demonstrated that the decrepitation process is very energetic and suggested the difficulty in containing these materials in a matrix. Based on this observation, it was expected that metal hydrides on the surface of the composite would be removed from the matrix during cyclic absorption/desorption tests.

Characterization The starting materials were characterized by particle size analyses. Decrepitated LANA0.75 powder (<45μm) was used to prepare the granules. The particle size distribution of the decrepitated LANA0.75 powders as measured on the particle size analyzer is shown in Figure 6. The relatively coarse copper powder was purchased as -40, +100 mesh. The results of the sieve analysis indicated that 90 wt. % of the powder was +100 mesh (>150μm) and that more than 99 wt. % of this powder was +170 mesh (>90μm). The other materials which were used in the development program were also characterized, however, the results are not included in this report.

A cross section of the metal hydride composite pellet after hydriding (Figure 7) indicates that the metal hydride granules are well dispersed in the copper matrix. The surface was vacuum impregnated with epoxy to fix the loosely bound LANA particles. The porosity content of the LANA granules appears to be approximately 50 volume percent but cannot be quantified accurately from micrographs such as the one presented in Figure 8.

There was no cracking observed in the pellet cross-section after 10 absorption/desorption cycles.

Metal Hydride Granules Porous metal hydride granules can be produced by forcing cold pressed metal hydride compacts through a series of sieves to obtain the granule size range. The granules can be vacuum sintered at temperatures high enough to provide sufficient strength for processing but low enough to limit densification. Composites containing the metal hydride granules produced by this method cracked after only one or two cycles. It was apparent that the granules did not have sufficient porosity to accommodate the expansion of the metal hydride without cracking the matrix.

From the above results, it was concluded that pore formers were necessary to create additional porosity in the metal hydride granules. For water soluble pore formers, the metal hydride particulates can be dispersed in a solution of the pore former dissolved in water. The mixture can be dried to leave the metal hydride particulates coated with the pore former. This material can be added to the matrix material using standard processing techniques and removed during sintering.

Several different water or alcohol soluble compounds were evaluated as pore formers, however, none were found to be acceptable. Compatibility problems, often with the decomposition products of the pore former were observed. In other cases, the pore formers were not completely removed

Very porous metal hydride granules can also be formed by blending metal hydride particles with a pore former available in a powder form, compacting the mixture, and forcing the cold-pressed compacts through sieves to form granules. Ammonium carbonate and its decomposition products were found to be chemically compatible in this composite system.

Ammonium carbonate decomposes slowly at room temperature. The granules have sufficient strength to remain intact during processing, however, it is important to process the granules rapidly to ensure that there is sufficient pore former remaining in the granules. The results of an isothermal thermogravimetric analysis of ammonium carbonate/LANA0.75 granules in flowing air at 26°C (Figure 9) indicates that all of the ammonium carbonate decomposes in less than eight hours.

In the specimens fabricated with ammonium carbonate as a pore former in the LANA0.75 granules, no cracking was apparent in the matrix after cyclic testing. A LANA0.75 to ammonium carbonate ratio of 4:1 by weight or approximately 50 volume percent was used in all of these tests. It may be possible to decrease the amount of pore former in the granules.

X-ray diffraction analysis confirmed that the LANA0.75 had not oxidized or separated prior to testing and that a hydride had formed during testing. Cyclic testing also indicated that the storage capacity and the absorption/desorption rates of the LANA0.75 were not affected during processing.

Matrix Materials Several different matrix materials and fabrication techniques were considered. High alumina cements, such as Sauereisen Paste #7®, were evaluated for use as a matrix material. Metal hydride composites were successfully fabricated by mixing LANA0.75/ammonium carbonate granules into a diluted slurry of the cement. It was necessary to maintain the temperature of the mixture at nearly 0°C to prevent the ammonium carbonate from decomposing. It was also necessary for the viscosity of the mixture to be high enough to keep the metal hydride granules in suspension. The suspension could be extracted with a pipette and dripped onto polished aluminum trays. After drying, the hardened droplets could be removed and vacuum outgassed in a small stainless steel chamber in a drying oven at 150°C. However, work on this process was abandoned because of the difficulty of maintaining the metal hydride granules in suspension during mixing and drying.

Cold compaction was selected as the most practical method of forming the composite. Uniaxial pressing resulted in acceptable microstructures. Isostatic pressing could be used if it is shown that a more uniform matrix density or decreased residual matrix stresses are advantageous.

Tests using an aluminum matrix were abandoned due to the difficulty of sintering aluminum. Although special precautions can be used to minimize the formation of the oxide, other metals could easily be substituted. Testing was done with nickel powders, however, the compacts had a very low green strength and had to be vacuum sintered at temperatures of 1200°C to 1300°C. Compacts made with copper powders had relatively high green strengths. The unsintered pellets could be handled and survived a 138 cycle absorption/desorption test with only minor degradation on the edges. It was shown that vacuum sintering can strengthen the copper matrix without affecting the ability of the composite to absorb hydrogen.

Matrix Microstructure It was demonstrated that the microstructure of the matrix is very important. The microstructure can be controlled by the form of the material being pressed. Cracking was a problem in the matrices fabricated from fine powders. Although fine powders result in very small porosity which is useful for containing the metal hydride, the fine powders also result in larger residual fabrication stresses in the compacts. Furthermore, the fine porosity apparently creates higher internal pressures in the composite which cause cracking during the desorption process.

Coarse powders have much better flow characteristics than fine powders and, hence, the compacts have smaller residual stresses. If extended cyclic testing indicates that the porosity resulting from the coarse matrix material is too large to effectively contain the metal hydride particles, a compromise such as granulated fines may be desirable.

The microstructure of the matrix can also be controlled by the weight of material loaded in the die assembly which has a fixed volume at closure. For most of the experiments the die charges were selected to result in a matrix density of ~85 of the theoretical density for the material. This selection was based on obtaining the greatest possible strength for the matrix while maintaining sufficient open porosity for the exchange of hydrogen.

Metal Hydride Loading Metal hydride granules on the surface of the nickel pellets were not retained by the matrix. During hydriding, small metal hydride particles from these granules were removed with the hydrogen flow. In these composites, the concentration of the metal hydrides must be sufficiently low to prevent the formation of continuous strings of metal hydride granules to the surface. Therefore, the metal hydride concentration is limited by the requirement that the metal hydride granules must be present as a discontinuous phase. Most of the pellets produced in this study had a Cu:LANA0.75 ratio of 6:1 by weight. This satisfied the minimum requirement for advanced TCAP of 0.4 kg of LANA0.75 per liter in the column based on a packing factor for right circular cylinders conservatively estimated at 0.55 based on previous studies.[11]

Sintering Sintering may be necessary for the copper matrix composites as was the case with the nickel matrix composites.

Sintering may be required to strengthen the pellets sufficiently for use in a TCAP column. The pellets were sintered in vacuum to prevent oxidation of the LANA. For most of these tests the pellets were contained in a quartz tube which had been evacuated to $<1 \times 10^{-5}$ torr and sealed. Attempts to sinter the pellets in helium were unsuccessful in preventing oxidation despite maintaining a positive pressure in the furnace chamber.

Vacuum sintering of the Sauereisen/LANA0.75 pellets at 1280°C resulted in a reaction between the matrix and the metal hydride. X-ray diffraction analysis indicated that the lanthanum and aluminum had oxidized and the nickel and silicon had reacted to form Ni_3Si. It was demonstrated that the excess water could be removed by heating to 150°C for four hours in vacuum without affecting the metal hydride.

Although the unsintered copper pellets survived cyclic testing with only minimal damage, it is likely that vacuum sintering will be required to increase the strength for use in a TCAP column. The strength of the copper-based composite can be increased by vacuum sintering. X-ray diffraction analysis (Figure 10) indicated that the LANA0.75 was unaffected by the vacuum sintering at 900°C for 2 hours.

Cyclic Absorption/Desorption Tests During the initial stage of the development program it was found that composites fabricated from metal hydride granules without pore formers began to fracture when the hydride formed during the first cycle.

The use of pore formers in the metal hydride granules eliminated the fracture problems in the matrix. Coarse nickel and copper powders were used to form the matrix for these composites. The sintered nickel matrix and unsintered copper matrix metal hydride composites did not fracture during the cyclic absorption/desorption tests in hydrogen. Quantitative testing also indicated that the storage capacity and the hydrogen absorption/desorption rates were acceptable. Many of the metal hydride particles from the granules exposed on the surface of the pellets were lost during the first few cycles. This eventually led to the formation of pits on the surface of the pellets (Figure 11).

Long-term testing (138 absorption/desorption cycles) on unsintered copper matrix composites demonstrated that only the metal hydrides on the surface of the composite were lost. Fine hydride particles were observed throughout the cross-section of the pellet (Figure 12).

Minor degradation was observed on the edges of some of the pellets. This apparently occurred in areas in which several granules were concentrated and exposed at an edge. These areas became very weak and it appeared that some matrix material was also lost, possibly during handling. The total weight loss after 138 cycles and handling was ~2.5% of the initial weight of the pellets. More than half of this loss occurred during the first five cycles and the subsequent handling prior to the long term test. This suggests that most of the metal hydrides could be removed from the surface of the pellet by cycling in hydrogen to create a more stable composite.

It was observed that matrices formed from fine copper powders were smeared on the edges of the pellets. Although pore formers were used to fabricate the metal hydride granules, it was observed that matrices fabricated from fine powders fractured during the desorption portion of the cycle. This cracking problem was attributed to the internal pressure in the composite pellet when the hydrogen gas Saureisen. It is likely that internal pressures were higher because of the finer porosity. Most of the cracking occurred at laminations on the side of the pellets indicating that the poorer flow of the fine powder may have resulted in greater internal stresses in the compact. Strengthening the matrix by vacuum sintering reduced the severity of the cracking but did not eliminate the cracking completely.

Coating The granules on the surface of the pellet were not retained by the matrix during cycling. Several preliminary cycles of hydriding could be performed prior to use to remove the metal hydride from the surface of the pellets. The composite could be improved by the development of a microporous coating to contain the metal hydrides on the surface of the pellet. This would eliminate the need to remove the exposed metal hydride granules prior to use. Preliminary coating development work is underway.

It was demonstrated that thin coatings, such as those produced by sputter coating, do not have sufficient mechanical strength to prevent the loss of the metal hydride granules on the surface of the composites.

Thicker, higher strength coatings were produced be electroless nickel plating. X-ray diffraction analysis confirmed that the coating was actually nickel phosphide rather than nickel. Phosphides are not compatible with LANA alloys and electroless nickel plating was abandoned.

The use of sol gel coatings on the copper matrix/metal hydride composites is being evaluated as method to retain all of the metal hydride material. Ideally, the microporosity of sol gel coating will allow hydrogen isotopes to penetrate freely and will contain the LANA0.75 granules on the surface of the pellet and will also retain the fine particles which form during decrepitation and migrate to the surface. Sol-gel coatings have been tested and appear to be fairly effective in containing the metal hydrides despite cracking and adhesion problems with the coating.

A coating may also be advantageous in increasing the metal hydride content of the composites. Without a coating, it will be necessary to limit the metal hydride content so the metal hydride does not form a continuous phase. Such a structure would allow the eventual removal of most of the metal hydride from the composite. In a coated metal hydride composite, it is expected that the metal hydride content would be limited by the matrix content necessary to provide sufficient mechanical strength in the composite.

COPPER/LANA0.75 PROCESS FLOWSHEET

The processing conditions presented in the process flowsheet in Figure 13 and described below result in a dimensionally stable composite. Additional studies will be performed to optimize these process conditions and to establish process limits.

Ammonium carbonate, which was originally in lump form, was ground and sieved to <45 µm. The ammonium carbonate powder was mixed with decrepitated LANA0.75 powder (<45 µm) and cold pressed into pellets to a density of ~3.5 g/cm^3.

The LANA0.75/ammonium carbonate pellets were forced through a series of sieves to granulate the material. Granules of >125 µm and <300 µm were used in the composite. Due to the high vapor pressure of the ammonium carbonate, the granules must be used immediately.

The LANA0.75/ammonium carbonate granules were mixed with coarse copper powder (-40 mesh, +100 mesh). This mixture was compacted to a fixed volume in a stainless steel die using a manual hydraulic press. A die charge of 0.460 to 0.470 g was used. A load of 2 to 3 thousand pounds was required to close the die. The loading and unloading rates could not be precisely controlled with the equipment used in this study. The typical pellet dimensions were 0.480 cm (+/-0.001 cm) for the diameter and 0.395 cm (+/-0.010 cm) for the height. These dimensions are provided for reference only and are not intended as production specifications.

The ammonium carbonate will evaporate in air at room temperature within two days based on weight loss measurements. The total weight loss due to evaporation was typically 0.04 g/pellet to 0.07 g/pellet. The composites can be used as-pressed, however, based on the results of the long-term cyclic test it appears that the pellets should be sintered to strengthen the matrix, particularly at the edges. The copper matrix pellets can be sintered in a vacuum ($<10^{-5}$ torr) at 900°C for two hours to strengthen the matrix.

The metal hydride on the surface of the pellets will not be retained by the matrix. If the coating development program is successful, a microporous coating will be used to contain the fine metal hydride particles. However, uncoated pellets can be cycled several times to remove the metal hydride particle from the surfaces. The actual number of cycles to remove the metal hydride from the surface will be determined as part of the optimization program.

CONCLUSIONS

- A process to fabricate dimensionally stable copper matrix-metal hydride composites was developed and successfully demonstrated.

- The composite pellets were cycled 138 times in hydrogen with the loss of LANA0.75 limited to that exposed on the surface of the pellet.

- Ammonium carbonate was very effective as a pore former in LANA0.75 composites in reducing the stress to the matrix during cycling in hydrogen.

- Copper matrix metal hydride composites can be used as-pressed, however, vacuum sintering will provide additional strength, which is needed particularly at the edges.

- If a coating is not successfully developed for these composites, most of the metal hydride particles exposed on the surface of the pellets can be removed by cycling several times in hydrogen.

FUTURE WORK

Several methods will be evaluated to minimize the loss of metal hydrides from the surface of the composite and to minimize the detrimental effects of this loss on the strength of the pellet. To improve the performance of the composite several methods such as vacuum sintering, substituting granulated copper fines for the coarse feed material, and using small charges of copper to cap the ends of the pellets will be evaluated. It is also likely that the edge degradation can be minimized by redesigning the die to produce radiused or chamfered edges.

The coating development program is focused on selecting a coating to retain the metal hydrides in the composite. Work is underway to improve the integrity of sol-gel coatings by controlling the drying rate. Electroless copper plated coating should also be evaluated.

Future work will be focused on optimizing the processing conditions for copper matrix composites. The size and volume of the matrix porosity can be controlled by the particle size of the feed powder, the pellet compaction pressure, and the sintering time and temperature. Similarly, the properties of the composites will be optimized by determining the optimum metal hydride content and the optimum porosity in the metal hydride granules. This will be important for other applications in which it will be desirable to increase the concentration of the metal hydride in the composite.

The testing program will be expanded to include more severe test conditions, tritium testing, and an evaluation of the separation efficiency. These tests will require greater quantities of the metal hydride composite pellets.

The final step in the development program will involve the scale-up of the process to produce kilogram quantities of the composite pellets. This will involve the use of automatic granulators, production scale blenders, and automated production presses. It is anticipated that most of this work will be subcontracted to an off-site vendor.

Additional applications for metal hydride composites will also be evaluated. The fabrication process is readily adaptable to substituting other metal hydrides. Other matrices can be used if necessary. It is likely that future applications will require increased metal hydride concentrations in the composite to satisfy weight or volume limitations.

REFERENCES

1. W. C. Mosley, DPST-87-446, "Early Stages of Decrepitation of Lanthanum-Nickel-Aluminum Alloys", June 12, 1987.

2. M. S. Ortman, L. K. Heung, A. Nobile, and R. L. Rabun, III, WSRC-RP-89-65, "Tritium Processing at the Savannah River Site (SRS): Present and Future (U)", October 23, 1989.

3. L. K. Heung, Disclosure No. SRS-91-028, "Method to Produce Stable Metal Hydride Compacts", October 5, 1990.

4. W. C. Mosley, SRL-HTS-90-007, HTS Monthly Report, "LANA-Bearing Material for Advanced TCAP", January 24,1991.

5. G. L. Enz, L.K. Heung, and G. G. Wicks, SRL-HTS-0227, "Preliminary Test of a Sol-Gel Method for Preparing a New Metal Hydride-Glass Composite.

6. H. Ishikawa, K. Oguro, A. Kato, H. Suzuki, and E. Ishii, Journal of the Less-Common Metals, 120 (1986) 123-133, "Preparation and Properties of Hydrogen Storage Alloys Microencapsulated by Copper".

7. Choong-Nyeon park and Reiner Kirchheim, J. of Alloys and Compounds, 182, (1992) 321-330, "A simple method of electroless copper plating for the preparation of metal hydride electrodes".

8. J. W. Congdon, Disclosure No. SRS-92-109, "Method to Produce Dimensionally Stable Metal Hydride Composites", January 14, 1992

9. Procedure Manual 1Q34, Nuclear Reactor Technology and Scientific Computations Department Quality Assurance Manual (U), January 1, 1991.

10. Procedure Manual 1Q43, DWP&HT Quality Assurance Procedure Manual (U), January 10, 1991.

11. B. W. Gamson, G. Thodos, & O. A. Hougen, Trans. Am. Inst. Chem. Eng., 39, 1, (1943).

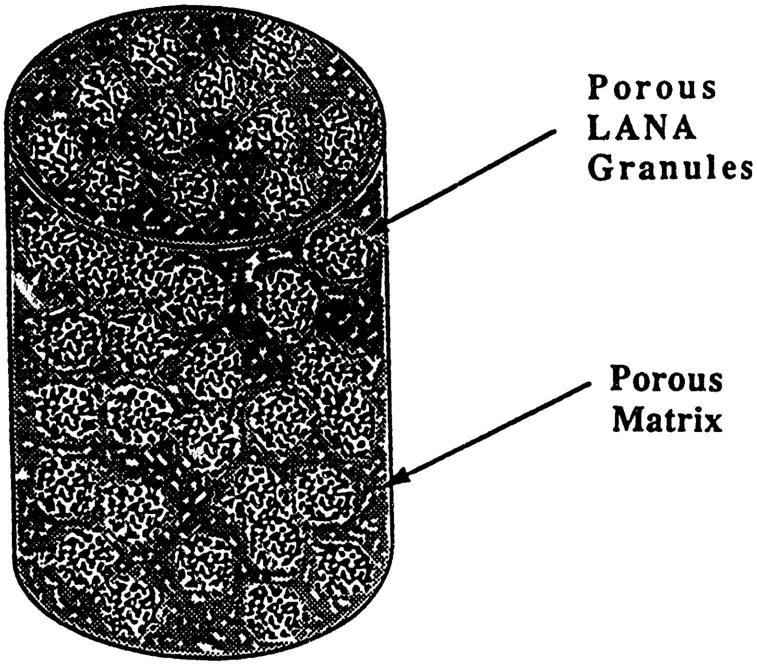

Figure 1: Proposed design for metal hydride composite.

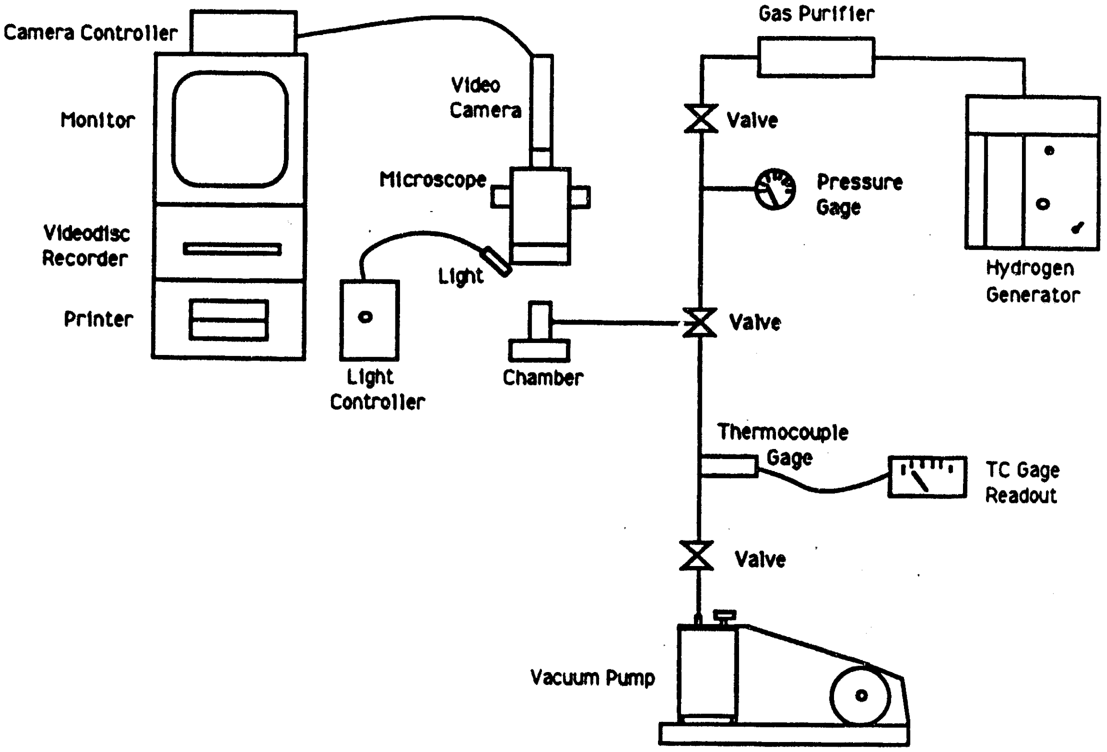

Figure 2: Schematic of apparatus for microscopic observation of metal hydride composites during cyclic absorption/desorption testing in hydrogen.

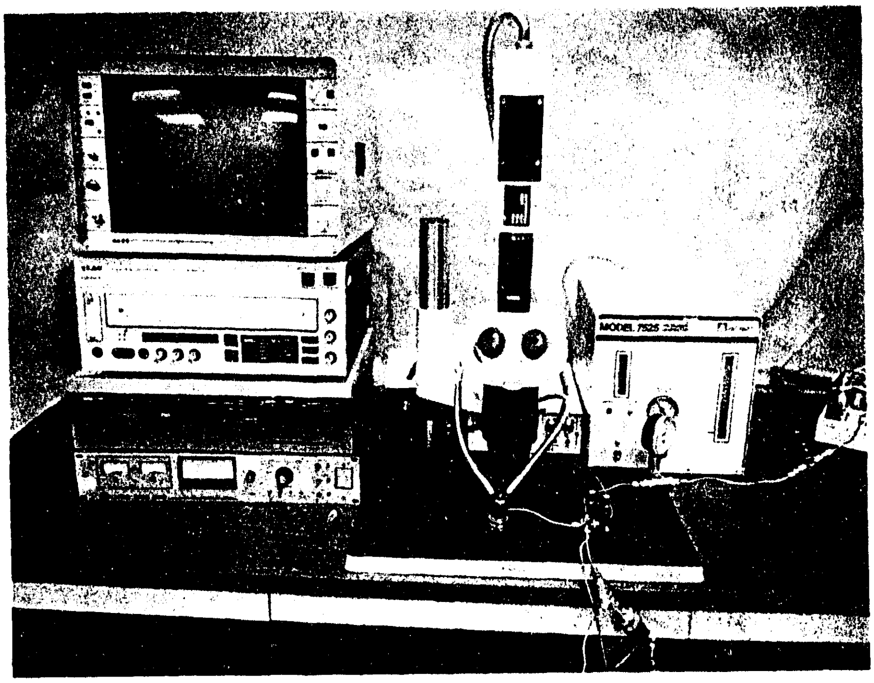

Figure 3: Photograph of apparatus for microscopic observation of metal hydride composites during cyclic absorption/desorption testing in hydrogen.

Figure 4: Top: As-received chunk of LANA0.75 (~1/4" dia.). Bottom: Cracking during hydriding (~30 seconds after crack initiation).

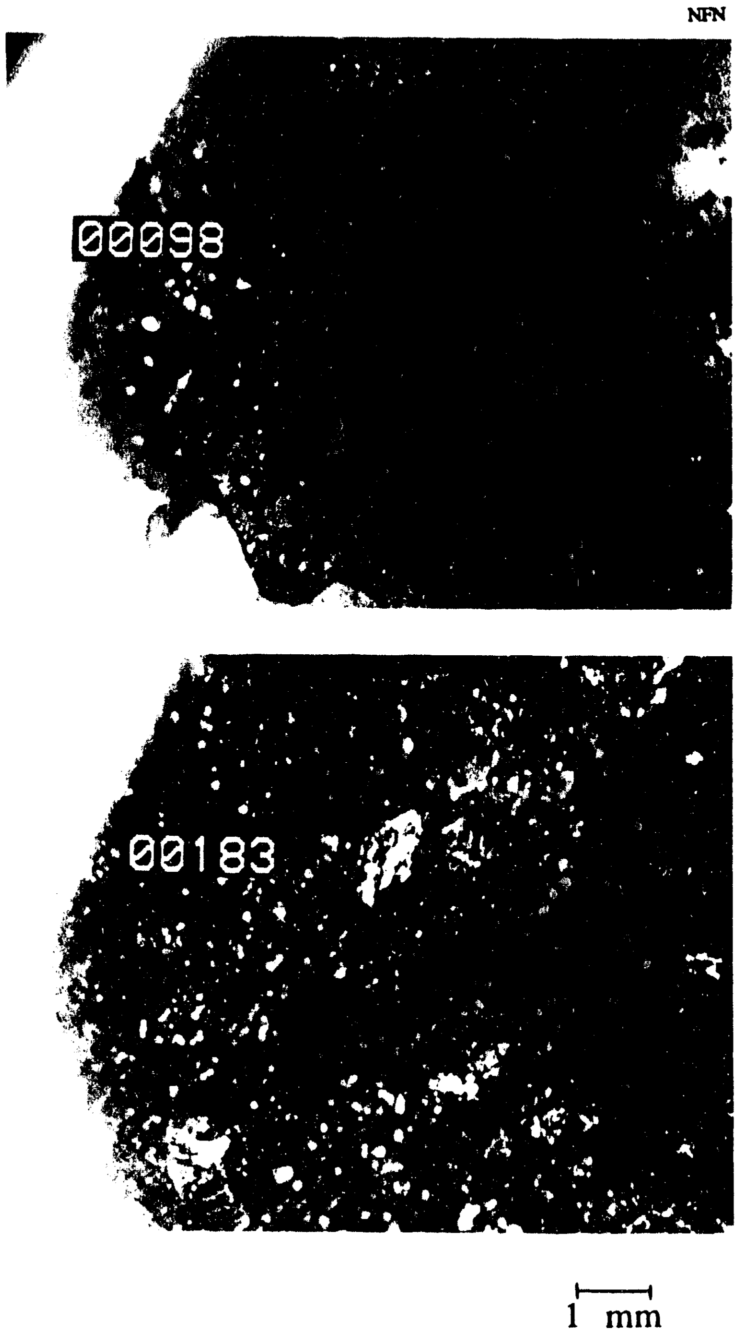

Figure 5: Cracking of LANA0.75 during hydriding
Top: ~1.5 minutes after crack initiation
Bottom: ~3 minutes after crack initiation

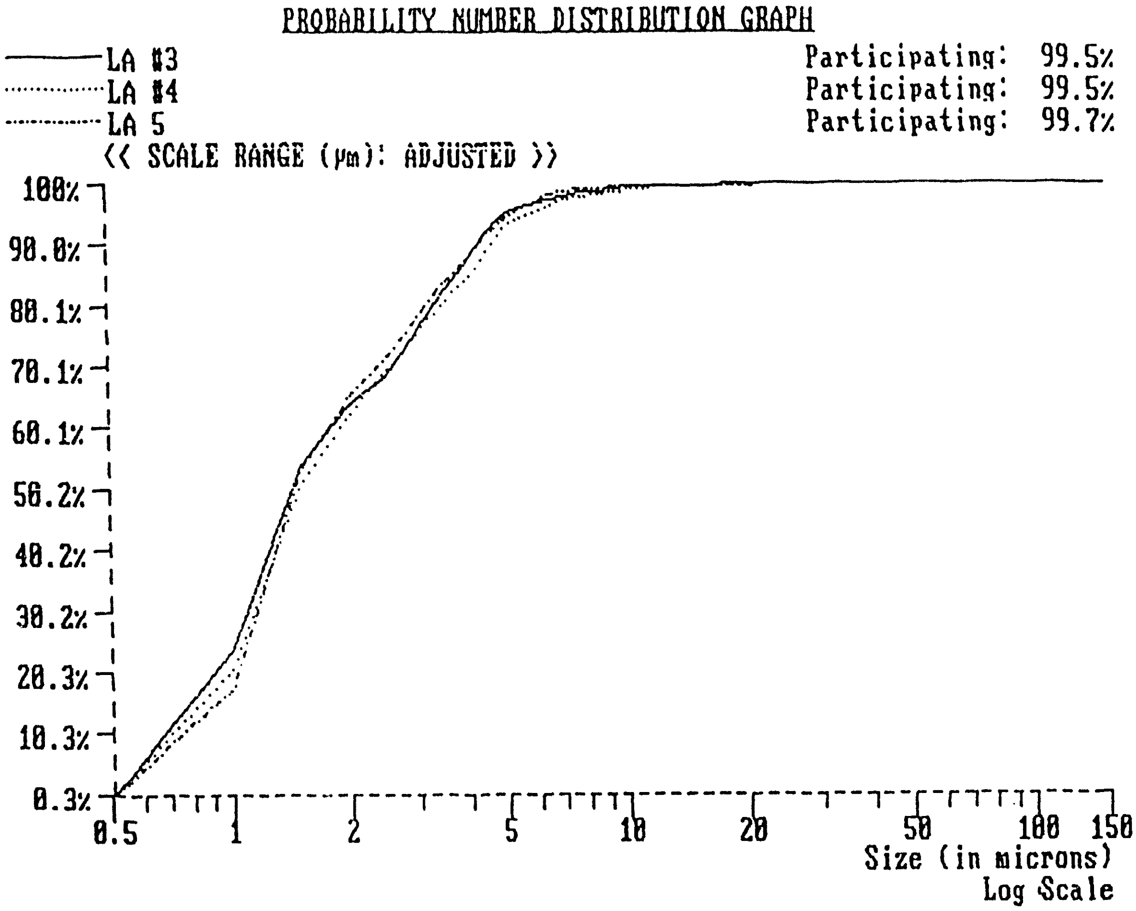

Figure 6: Particle size distribution of decrepitated LANA0.75 as obtained from the Brinkman Particle Size Analyzer.

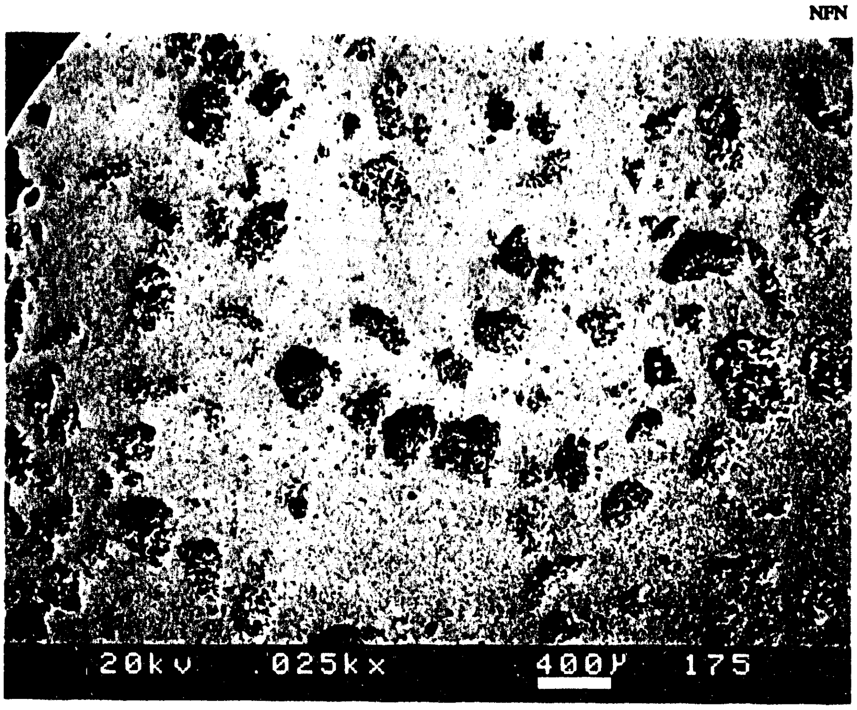

Figure 7: Cross-section of copper/LANA0.75 pellet indicates that the granules are well-dispersed and are a discontinuous phase.

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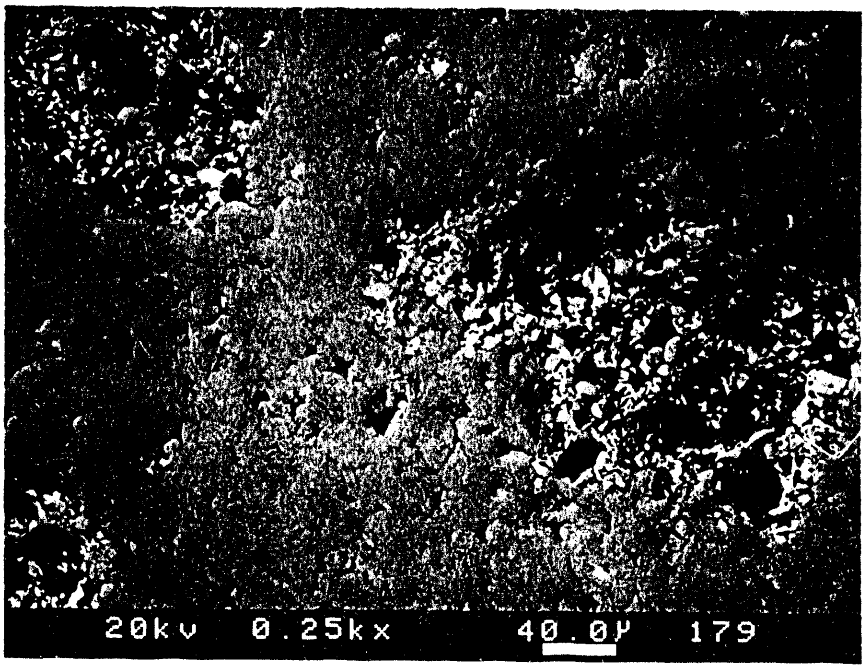

Figure 8: Microstructure of copper/LANA0.75 composite after 10 absorption/desorption cycles.

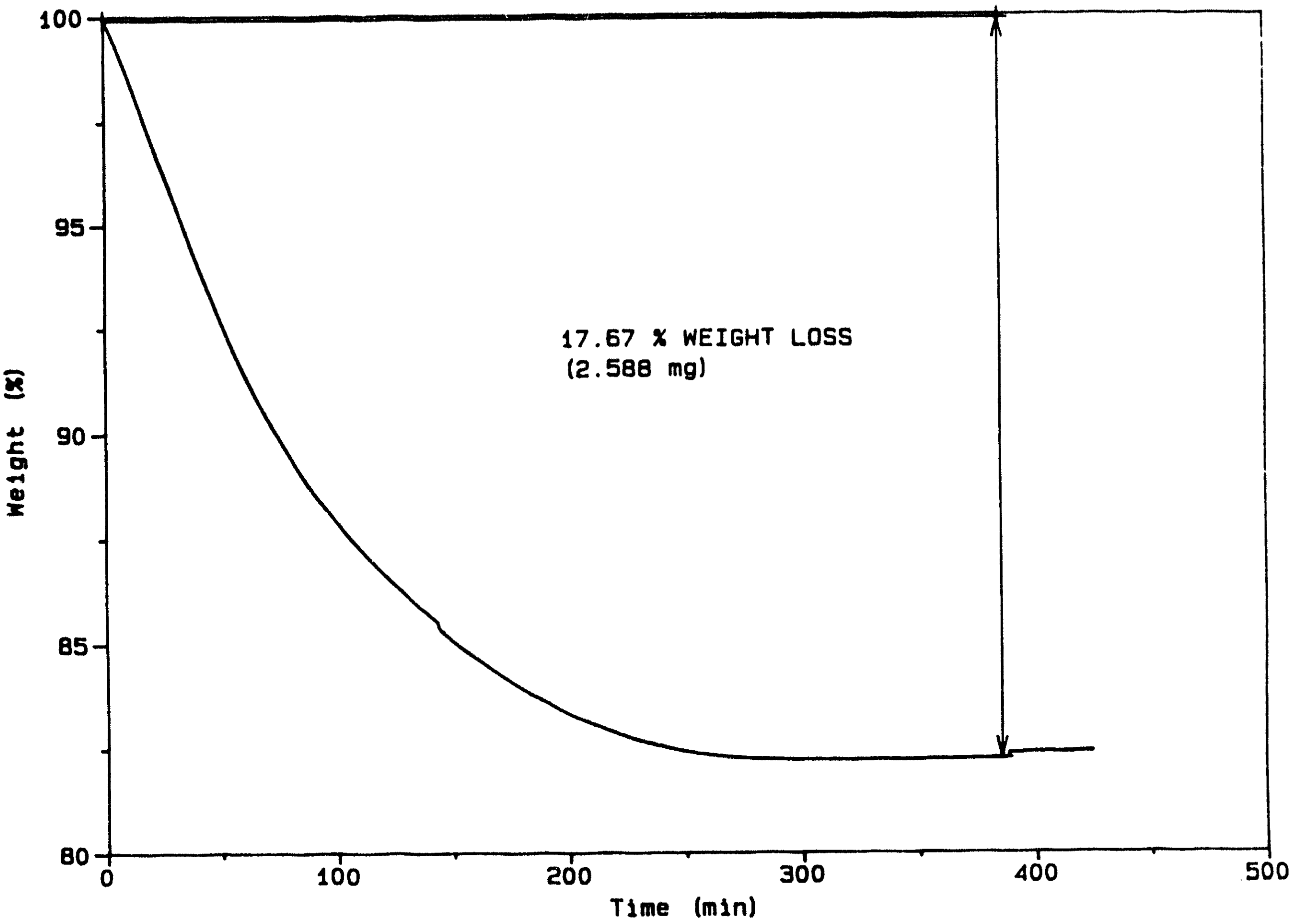

Figure 9: Isothermal thermogravimetric analysis of 20 wt. % ammonium carbonate/LANA0.75 granules in flowing air at 26°C. Note: The analysis was initiated approximately 20 minutes after the granules were fabricated which accounts for the differential between the measured weight loss (17.67%) and the expected loss (20%)

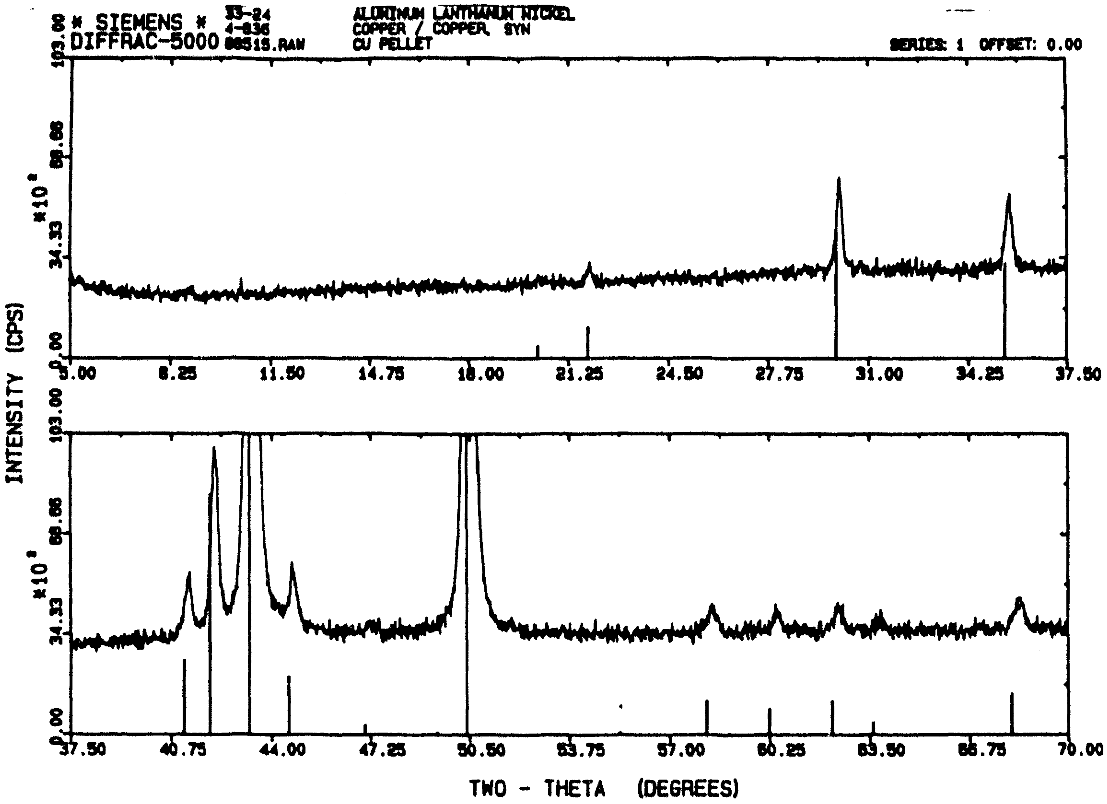

Figure 10: X-ray Diffraction Analysis of Cu/LANA0.75 pellet after vacuum sintering at 900°C for 2 hrs. indicates that the LANA0.75 did not oxidize or react with the copper.

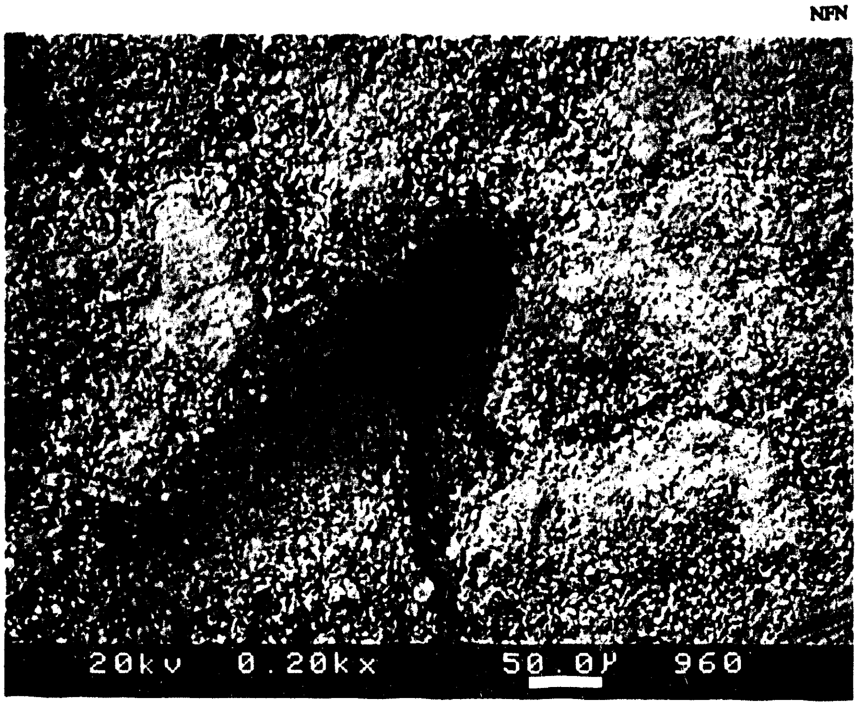

Figure 11: SEM micrograph of end surface of unsintered Cu/LANA0.75 pellet after 138 absorption/desorption cycles. Pit was formed by the loss of metal hydride from a granule exposed on the surface of the pellet.

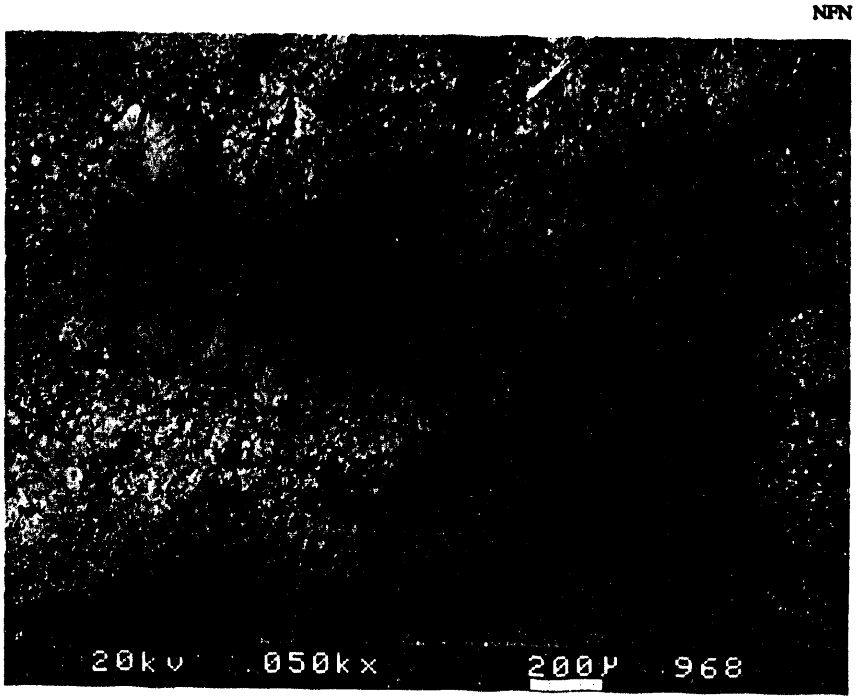

Figure 12: Cross-section of composite after 138 absorption/desorption cycles indicates that metal hydrides in the interior are retained. SEM micrograph of fracture surface of unsintered Cu/LANA0.75 composite pellet. Note: the fine particles are the metal hydrides.

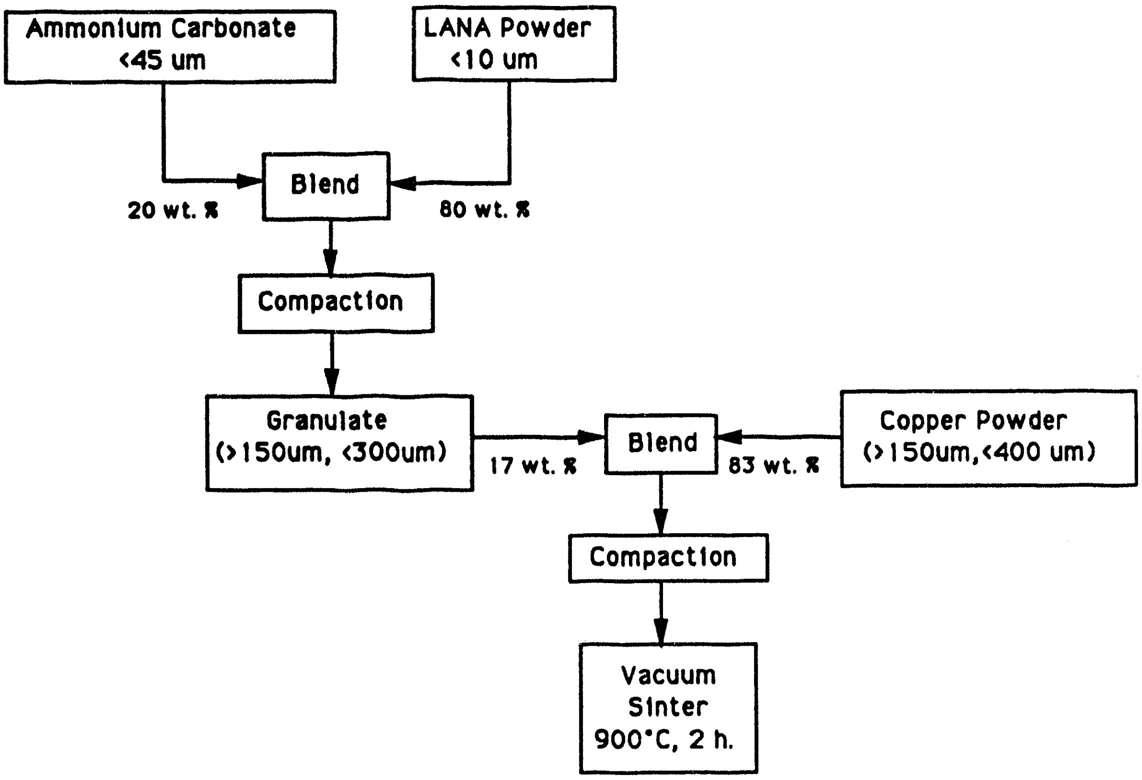

Figure 13: Process flowsheet for the fabrication of metal hydride composites.

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