Thermal Stability Testing of LANA.75

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Savannah River Site has used the metal hydride $LaNi_{4.25}Al_{0.75}$ (LANA.75) in the Tritium Facilities for over two decades. LANA.75 beds store significant quantities of tritium but have a limited service life due to the radiolytic decay of tritium to ^{3}He within the metal matrix. It has been shown that isotherm performance of a tritium-aged LANA.75 sample can be restored by heating under vacuum. Additional investigation is needed to ensure there are no unexpected changes to the hydride before this technique is employed in full scale beds in the Tritium Facilities. In addition, it is necessary to verify the regenerable behavior and thermal stability of LANA.75 on a small scale prior to it being implemented on a large scale.

A non-tritiated bench-scale LANA.75 sample was held at 750 °C under vacuum for 200 hours to simulate exposure to multiple restoration evolutions. Hydride isotherm performance, particle size distribution, chemical composition, crystallinity, and morphology are compared between the pre- and post-restorative testing samples. No significant changes were observed in particle size, composition, or crystallinity. Comparison of pre- and post-anneal isotherms showed that performance improved rather than deteriorated during the evolution. Scanning Electron Microscopy (SEM) analysis showed small growths on the particle surface after exposure to regeneration conditions. Additional testing will be required to determine the cause of these growths.

Keywords: hydrogen; hydrogen storage; regeneration

I. INTRODUCTION

Savannah River Tritium Enterprise (SRTE) has used $LaNi_{4.25}Al_{0.75}$ (LANA.75) as a hydride to store tritium for over two decades. The hydride beds store significant quantities of tritium but have a limited service life due to the radiolytic decay of tritium to ^{3}He within the metal matrix. ^{3}He is larger than atomic hydrogen and has a very low solubility in the metal so it becomes trapped and alters the crystal structure of the hydride. The altered structure, in turn, causes the formation of a heel of trapped hydrogen isotopes and reduces the reversible capacity of the hydride under normal processing conditions. [1, 2] With sufficient tritium exposure, the bed will lose its ability to deliver ^{3}He-free tritium. Whenever a bed's reversible capacity impacts the process throughput or the bed can no longer deliver 3He-free tritium, it must be replaced at significant cost and effort to the facility. Typically, after 8-12 years of service, depending on their location in the facility, beds need to be replaced.

One strategy to reduce the cost and effort of having to replace the beds is to regenerate the beds in place. Nobile et al. [3] saw that the ^{3}He that was produced in the lattice due to the radiolytic decay from tritium did not leave the lattice and caused (1) decreased tritium desorption pressures, (2) increased slopes of the desorption isotherm plateau, and (3) small quantities of irreversibly-held tritium. However, those effects were partially reversed by briefly heating the samples to 350 °C. Staack et al. [4] showed that the majority of the ^{3}He was released in two separate peaks (one near 220 °C and the other near 490 °C). By the time they had reached 600 °C, the bulk of the gas from a tritium-aged sample had been released. Staack and James [5] showed that heating a tritium-aged LANA.75 sample to 450 °C moderately restored the performance while heating the sample to 600 °C significantly improved the performance. This improvement between 450 and 600 °C was likely due to the release of the second ^{3}He peak. They were, then, able to successfully demonstrate the regeneration of a tritium-aged sample and restore the performance to near "virgin" values by heating the material to 750 °C. In addition, they noticed that the "regenerated" samples had a plateau pressure higher than anticipated.

Based on the performance results from Staack and James, [5] this project tested the performance of a non-tritiated LANA.75 sample prior to and following an extended time at an elevated temperature. The project was also used to determine whether the post-regeneration elevated plateau pressure was due to tritium decay or the regeneration procedure itself. Various analyses were performed to verify the chemical make-up and crystallinity of the sample.

II. EXPERIMENTAL PROCEDURE

II.A. Sample Information

The LANA.75 alloy used for testing was purchased from Japan Metals and Chemicals, USA. Initial characterization of this material was performed by Shanahan. [6]

II.B. Test Apparatus

The Manual Manifold 1 (MM1) is a manifold located in the Applied Research Center (ARC) lab used for characterizing the interactions of non-radioactive hydrogen isotopes (protium and deuterium) with various hydrides. A schematic of the MM1 apparatus is shown in Figure 1. MM1 has two separate sides, Manifold A and Manifold B, that can be isolated from one another and, thus, run simultaneously. Each side contains three (3) calibrated expansion volumes as well as other analytical components. A nickel block is used to facilitate uniform heating of the sample. The heater block includes bores for placement of thermocouples, and a proportional-integral-derivative (PID) controller is used for control and overtemperature protection. Heat is provided by three (3) 300-Watt cartridge heaters set into the block. Hydrogen is supplied from gas supply cylinders at 99.9999% purity. ***[Figure 1 near here]***

A novel test cell was designed and fabricated to accommodate the high temperatures required for the thermal testing. A 200 cm^3 unheated buffer volume was added to the small sample cell to ensure that the design pressure of the entire test cell would not be exceeded at high sample temperatures. The test cell assembly is shown in Figure 2. ***[Figure 2 near here]***

II.C. Method

Hydrides can be compared using pressure vs. composition graphs of the metal hydride/gas system collected with the sample at constant temperature (isotherms). The composition of a hydride is typically expressed as the hydrogen-to-metal atomic ratio (Q/M, where Q = the sum of all hydrogen isotopes). For an absorption isotherm, equilibrium pressure measurements are taken after an aliquot of gas is added to the system. Likewise, for a desorption isotherm, equilibrium pressure measurements are taken after an aliquot of gas is removed from the system. The quantity of hydrogen absorbed or desorbed by the hydride is inferred from the change in pressure measurements of the gas phase.

To begin the experiment, the sample (approximately 5 g) was loaded into the sample cell. At the same time, some of the virgin material was recovered for laboratory analyses. The LANA.75 material was activated in the sample cell by fully loading the sample at 80 °C in a single step by expanding protium in the adjacent volume into the test cell and allowing the sample to equilibrate at a pressure above the plateau pressure. After the material equilibrated with the protium, the test cell temperature was kept constant at 80 °C while being evacuated to a pressure below the plateau pressure. This process was repeated for a total of 10 times. Cycling the hydride causes the particulates to swell and shrink, fracturing the particulate into smaller pieces. This process produces fresh surfaces, which triggers faster kinetics in the material. After the material had been activated, the sample was reloaded. Then, a verification desorption isotherm was run to ensure the material performance was similar to that determined by Shanahan. [6]

After obtaining the verification desorption isotherm, the material was passivated by introducing small aliquots of air into the test cell. Once the temperature and pressure stabilized due to the introduction of air to the sample, the manifold and test cell were evacuated. This procedure was repeated until there was no noticeable difference in the final temperature and pressure between cycles, indicating that it was no longer air sensitive. The test cell was then opened, and a portion of the pre-anneal material (approximately 1.5 g) was recovered for additional analyses.

The remaining material (approximately 3.5 g) in the sample cell was re-activated at 80 °C by loading and unloading three times with protium as shown by Shanahan and Klein. [7] Once re-activated, pre-anneal desorption isotherms at 80, 100, and 120 °C were collected.

After the pre-anneal desorption isotherms were completed, the hydride was annealed. The sample cell was heated under vacuum (absolute pressure less than 1 torr) to 750 °C and held for a total of 200 hours over two weeks – the system was under vacuum continuously for 2 weeks, but the heat was removed during the weekend. After reaching 200 hours of annealing time, the sample cell was cooled and the material was reloaded so that a new set of desorption isotherms could be collected at 80, 100, and 120 °C. Following the post-anneal desorption isotherms, the sample was passivated so that a portion of the post-anneal material (approximately 1.5 g) could be collected for additional analyses.

III. RESULTS AND DISCUSSION

III.A. Isotherms

Following initial activation, a desorption isotherm at 80 °C was performed on the LANA.75 material to verify that it had the same behavior as the previous JMC sample tested by Shanahan. [6] The verification isotherm showed that the material behaved similarly to the previous JMC sample.

After passivation, recovery of a portion of the activated pre-anneal sample, and re-activation of the remaining sample, additional desorption isotherms were collected at 80, 100, and 120 °C. A second isotherm was collected at 120 °C to show reproducibility of the system. These isotherms are shown in Figure 3. The isotherms showed a slightly sloped plateau at all temperatures, and the second isotherm at 120 °C showed that the experiment was reproducible. ***[Figure 3 near here]***

The final set of desorption isotherms were collected after the annealing process. Isotherms were collected at 80, 100, and 120 °C. These isotherms, along with the pre-anneal isotherms, are shown in Figure 4. The post-anneal isotherms have a similar shape in the α and β phases and have similar transition points to/from the plateau as the pre-anneal isotherms. However, the plateau regions for each temperature are flatter for the post-anneal material. This change in plateau suggests that the post-anneal material is more homogenous than the starting material. ***[Figure 4 near here]***

Another difference noted between the isotherms is that there appears to be a slight heel in the α region in the post-anneal material. This is shown in the isotherms at 100 and 120 °C. However, it does not appear in the isotherm at 80 °C. This is likely due to accumulation of small errors in the pressure, temperature, or volume measurements during isotherm collection.

III.C. Elemental Analysis

Elemental analysis was performed via inductively coupled plasma emission spectroscopy (ICP-ES). The Leeman Prodigy ICP-ES provides multi-elemental analyses of solutions. Measurements are based on atomic emission from excited atoms and ions. Liquid samples are nebulized, and the aerosol produced is transported to an argon plasma. In the high temperature plasma (10,000 K) atomic species are excited to higher energy states resulting in characteristic atomic and ion line emission. The spectra are dispersed through a grating spectrometer (polychromatic). The intensities of the lines, which are directly proportional to analyte concentration, are monitored by a Large Programmable Array Detector (L-PAD). The photocurrents from the L-PAD are processed, quantified and controlled by a computer system. A small amount (0.05 to 0.26 g) of the LANA material is dissolved in a few millilitres of concentrated HCl, which is then diluted to 50 mL of solution. The ICP-ES results, as seen in Table I, show that the composition is very close to the expected value when La is forced to 1.00. This result corresponds with Shanahan. [6]

[Table I near here]

Prior to each sample being run on the ICP-ES, a blank sample was run. Thus, any contaminants could be identified when the sample was tested. All three samples detected both Ca and Mg present above the instrument detection limits. However, concentrations for both were 3-5 orders of magnitude lower than those for La, Ni, and Al. Therefore, they were not included in Table I.

III.D. X-ray Diffraction Analysis

X-ray diffraction is a scattering of X-rays by the atoms of a crystal that produces an interference effect. The resulting diffraction pattern provides information on the structure of the crystal or the identity of the crystalline substance. For this analysis, the LANA.75 material was ground in ethanol using an agate mortar and pestle into a fine powder until the particle size was somewhere between 10-50 μm. The ground powder was attached to a plate glass slide using a Collodion/Amyl Acetate solution. The X-ray diffraction data were collected on a Bruker D8 X-ray Diffractometer by step scanning over the 2Θ range of 5-70° with a step size of 0.02° and a dwell time of 1 second.

The spectra shown in Figure 5 indicate that there were no material changes between the virgin, pre-anneal, and post-anneal materials. In addition, there were no spurious peaks detected, and the observed peaks were sharp. ***[Figure 5 near here]***

The ICP-ES results showed that there was very little contamination in the material. For XRD spectra, contaminants, either other phases, or elements, would lead to extra peaks and/or peak shoulders. This was not observed in the XRD spectra in Figure 5. Thus, this result reinforced the ICP-ES result that there was little to no contamination of the material.

III.E. Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy Analysis

The scanning electron microscope (SEM) produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample providing information about the surface topography and composition of the sample. A Carl Zeiss Microscopy LLC Sigma VP field emission scanning electron microscope (FE-SEM) was used to image these samples. It is equipped with secondary electron, backscattered electron, and in-lens secondary electron detectors. It has an imaging capability up to 500,000X.

Energy dispersive X-ray spectroscopy (EDS) is an analytical technique used for elemental analysis or chemical characterization of small surfaces of a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing a unique set of peaks in its electromagnetic emission spectrum. For the Carl Zeiss SEM, the EDS is performed using an Oxford Instruments X-Max 20 silicon drift detector to detect elements greater than atomic number 3 (Z>3). EDS data and maps are analyzed by Oxford Instruments' INCA 4.15 data analysis software.

Figures 6, 7, and 8 show several SEM images of the virgin, pre-anneal, and post-anneal material. One observation from the images is that the virgin material is much larger than either the pre-anneal or post-anneal material. The scale shown on the image of the virgin material (Figure 6) is an order of magnitude larger than the images of the pre-anneal (Figure 7) and post-anneal material (Figure 8). Another observation is that the virgin material does not have any cracks. The smaller size and the cracks seen on the pre-anneal and post-anneal material is due to the volume changes caused by the absorption and desorption of hydrogen. ***[Figures 6, 7, and 8 near here]***

A difference is seen between the pre-anneal and post-anneal materials. The image for the pre-anneal material appears to be sharper (i.e., less fuzzy) than the image for the post-anneal material. When the magnification is increased on the post-anneal material (see Figure 9), it becomes evident that growths have developed on the particle surface at some point between sample recoveries. The appearance of the growths was unexpected, but they did not appear to adversely impact the isotherm performance. ***[Figure 9 near here]***

EDS was performed by focusing 20 kV electrons on specific areas of the SEM image. All the spectra show lanthanum (La), nickel (Ni), and aluminium (Al) along with some carbon (C) and oxygen (O) present. Carbon is due to the epoxy from the sticky tape that is used to hold the particles. Oxygen is likely from oxides on the surface of the metal that are formed during sample passivation with air. EDS was performed on the surface of the material as well as the growths. The growths tend to have a higher oxygen content than the surface. It is assumed that this happened either during the reactivation step or the simulated regeneration. It is unknown whether these growths are due solely to temperature or rearrangement of lanthanum, nickel, or aluminum oxides formed during passivation.

IV. CONCLUSIONS

LANA.75 was heated under vacuum to 750 °C for 200 hours, bounding the maximum expected time a regenerable bed would be exposed to regeneration conditions. The pre-anneal and post-anneal isotherms have a similar shape in the α and β phases and similar transition points to/from the plateau. However, the plateau regions for the post-anneal material are flatter than that for the pre-anneal material. A flatter plateau suggests that the material is more homogeneous than the pre-anneal sample. ICP-ES showed no significant changes in elemental composition due to the heat treatment. Particle size analysis showed that the pre-anneal and post-anneal material were similar in size. The growths on the post-anneal material were unexpected but did not appear to adversely impact isotherm performance and should not inhibit regenerable bed development.

Additional testing will be performed to determine whether the growths are related to sample passivation or heat treatment. Operational beds are not expected to be repeatedly passivated and re-activated. If the growths are due to prolonged exposure to elevated temperatures, the targeted regeneration temperature can be reduced to prevent growth formation.

V. ACKNOWLEDGEMENT

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Table I. LANA.75 Composition when La is forced to 1.0.

	Composition
Virgin Material	$La_{1.00}Ni_{4.21}Al_{0.77}$
Pre-Anneal Material	$La_{1.00}Ni_{4.20}Al_{0.74}$
Post Anneal Material	$La_{1.00}Ni_{4.24}Al_{0.72}$

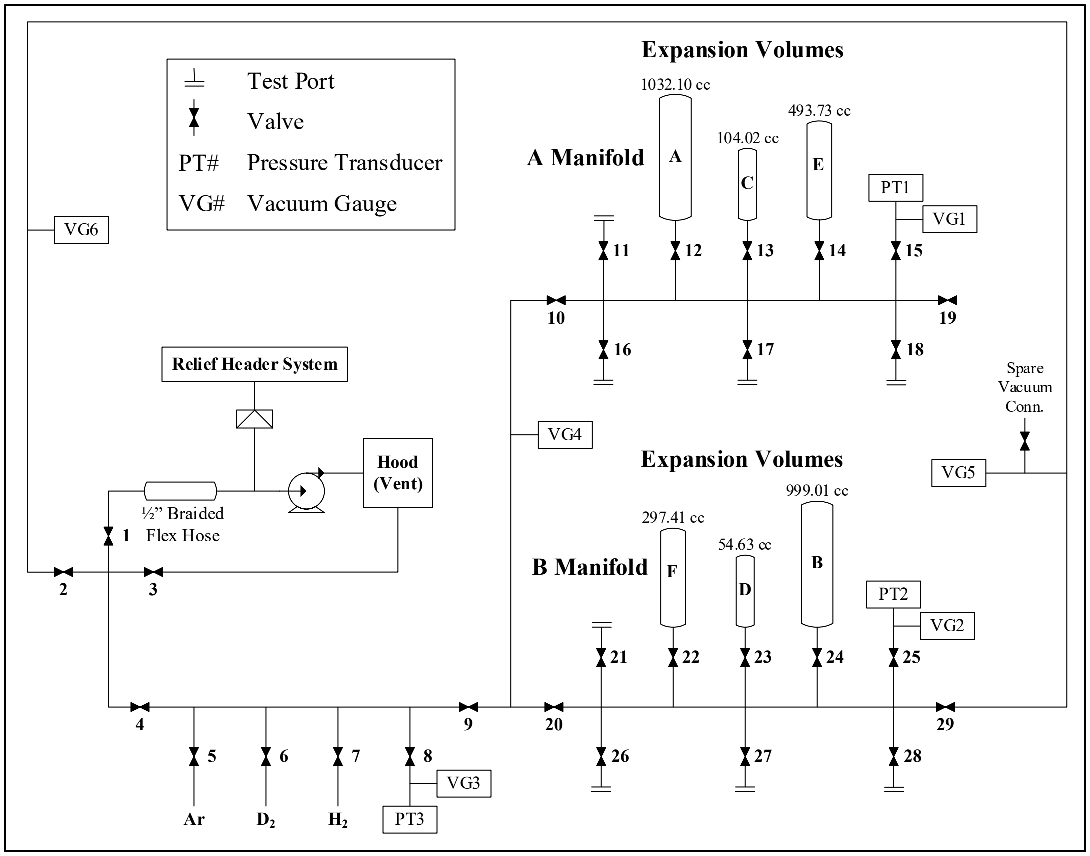

Figure 1. Schematic of Manual Manifold 1 (MM1).

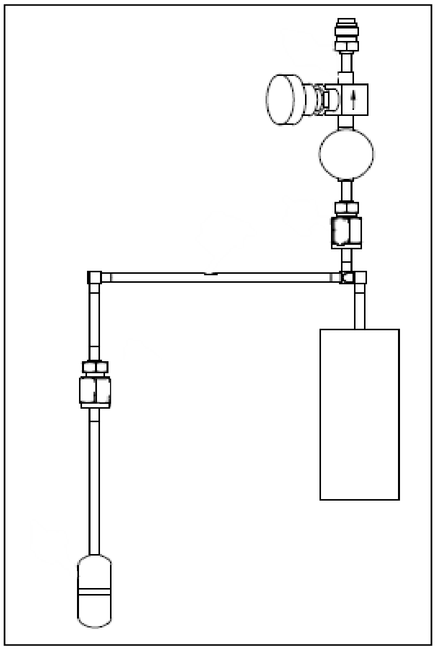

Figure 2. Diagram of novel test cell for thermal stability testing.

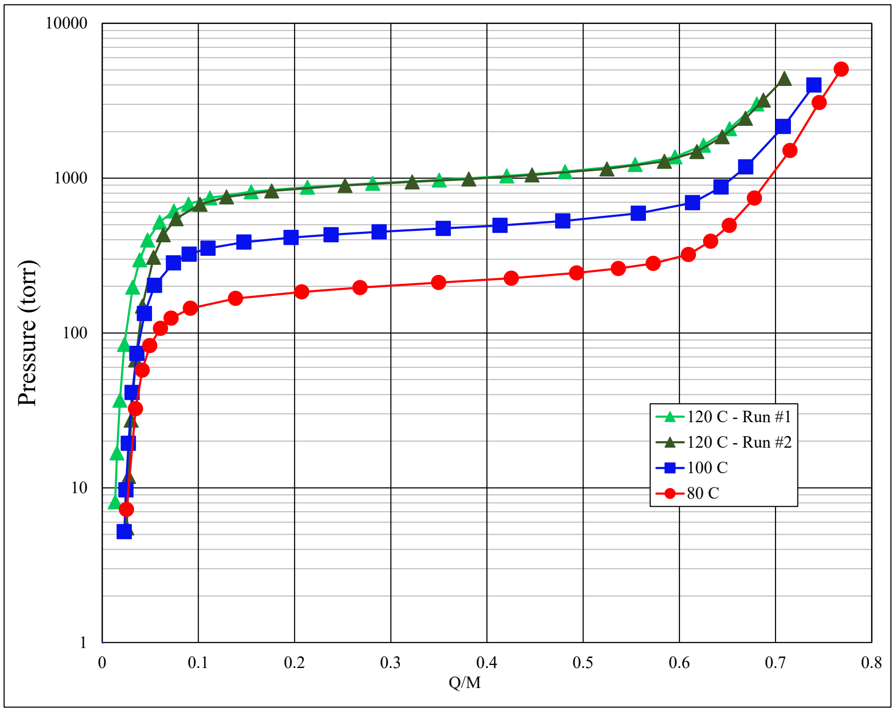

Figure 3. Pre-anneal isotherms of LANA.75 at 80, 100, and 120 °C.

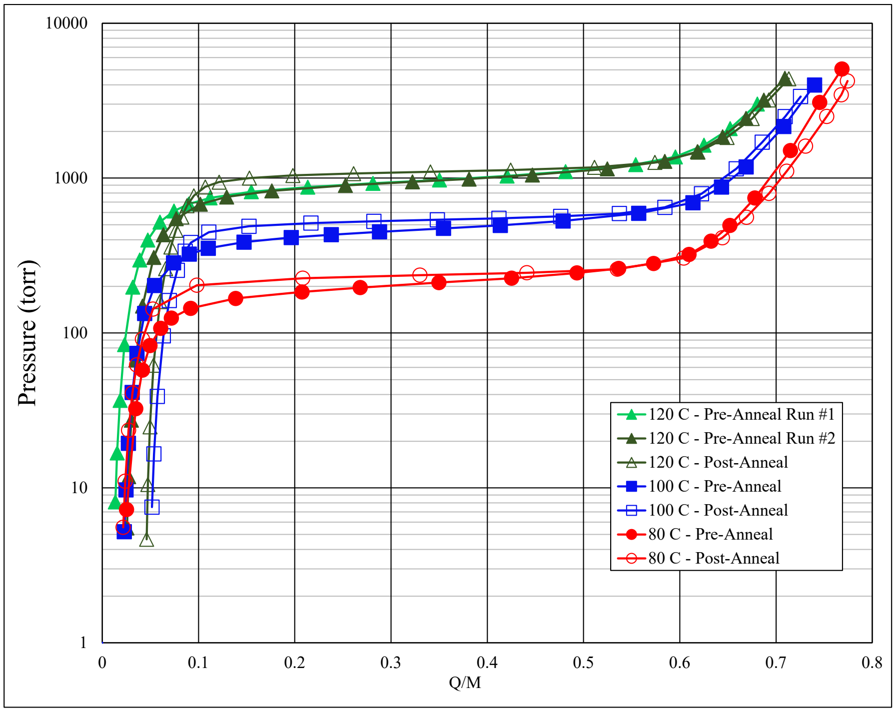

Figure 4. Comparison between LANA.75 pre-anneal and post-anneal isotherms.

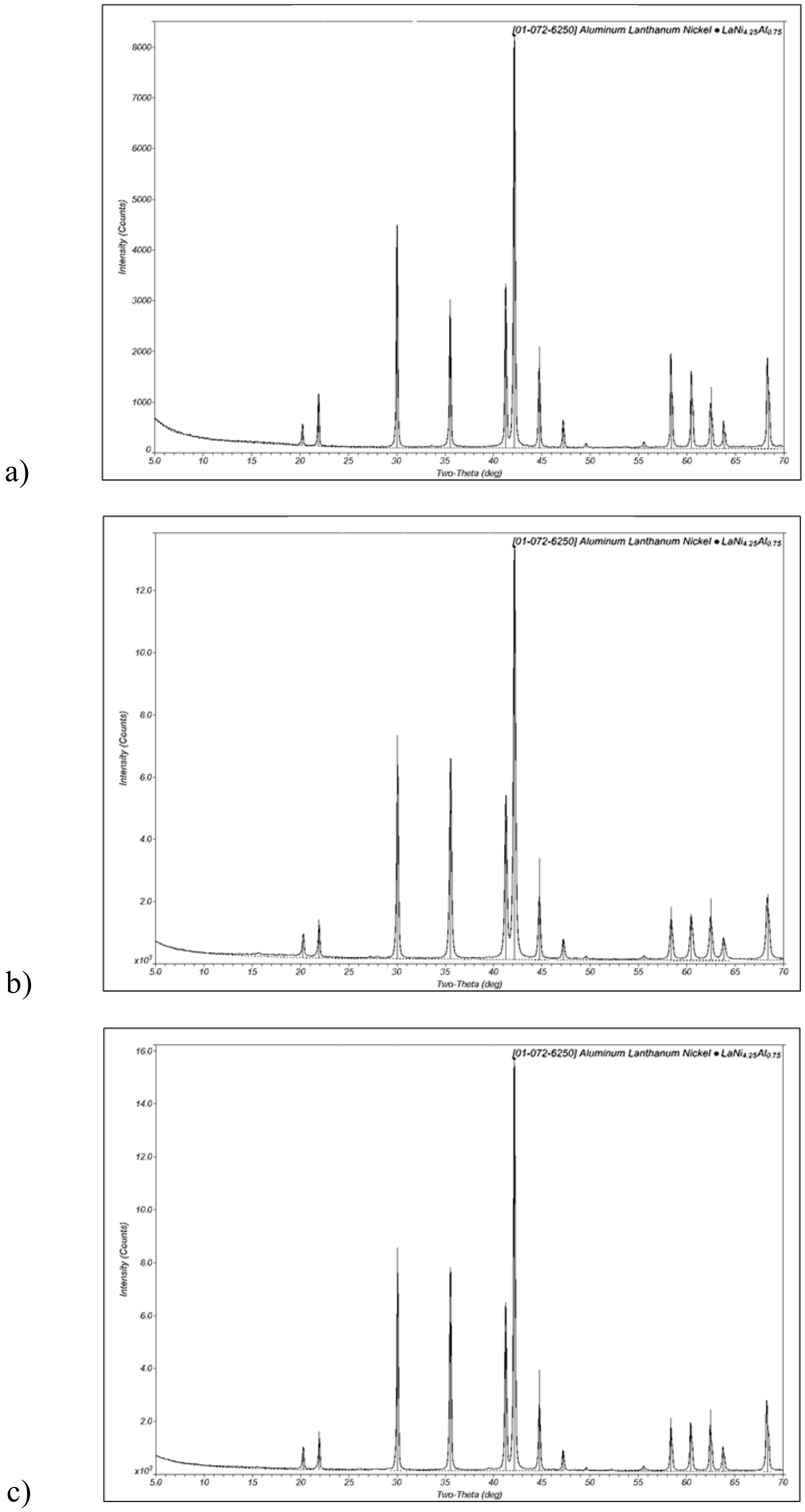

Figure 5. XRD patterns for a) virgin material, b) pre-anneal material, and c) post-anneal material.

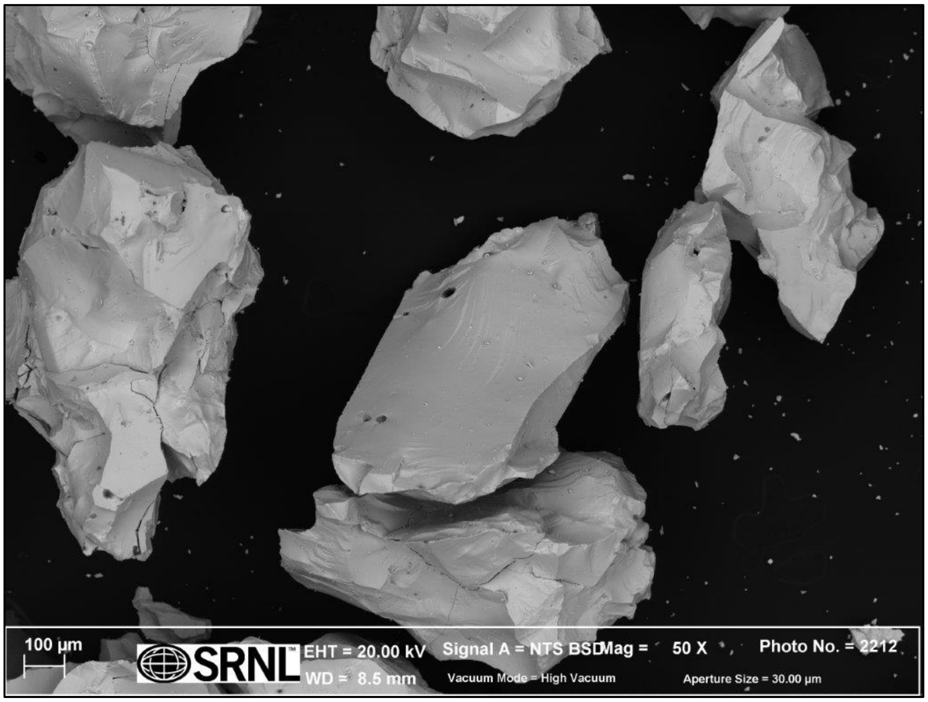

Figure 6. SEM images of virgin material at 50X magnification.

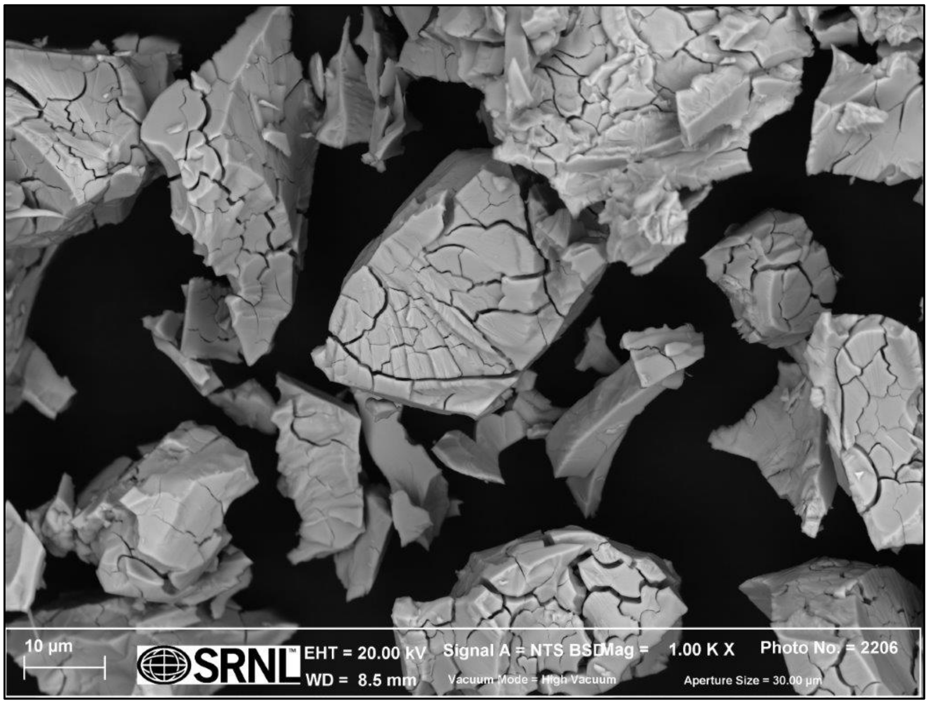

Figure 7. SEM images of the pre-anneal material at 1,000X magnification.

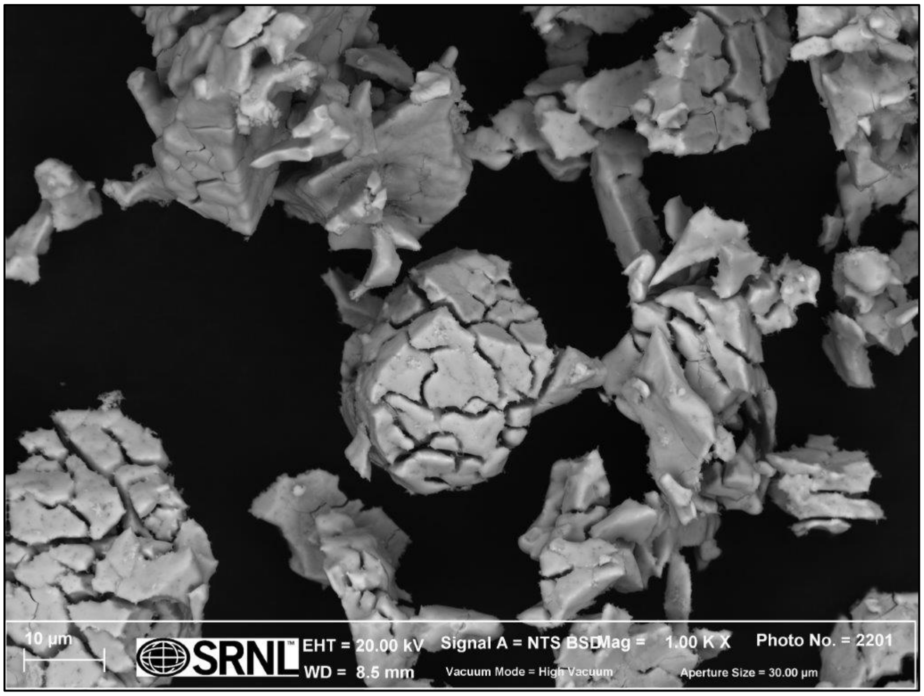

Figure 8. SEM images of the post-anneal material at 1,000X magnification.

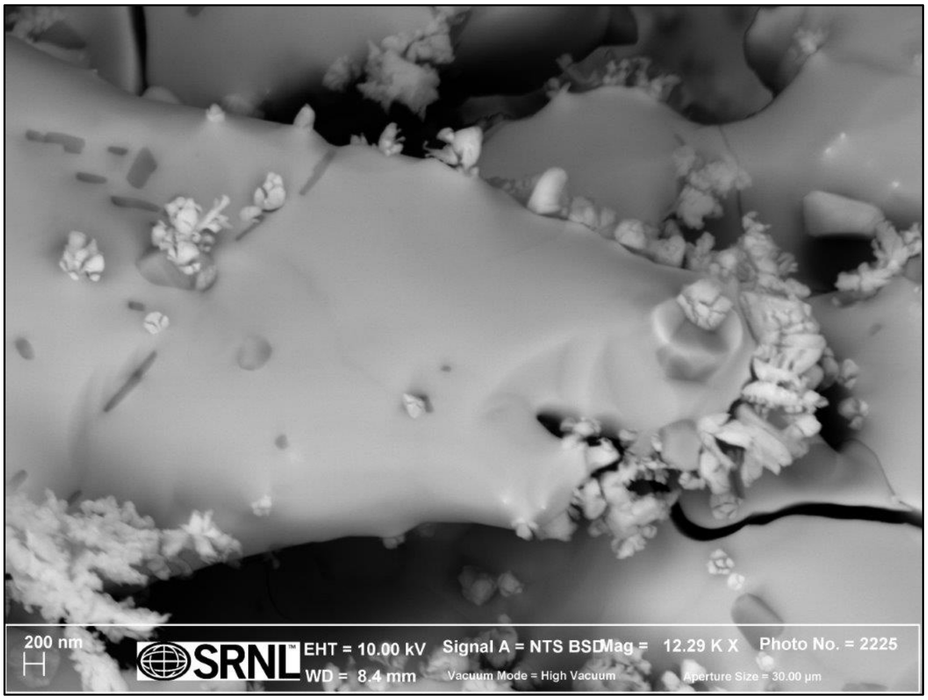

Figure 9. SEM image of LANA.75 post-anneal material at a magnification of 12,290X.