

BENEFITS OF RAPID SOLIDIFICATION PROCESSING OF MODIFIED LaNi_5 ALLOYS BY HIGH PRESSURE GAS ATOMIZATION FOR BATTERY APPLICATIONS

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ABSTRACT

A high pressure gas atomization approach to rapid solidification has been employed to investigate simplified processing of Sn modified LaNi_5 powders that can be used for advanced Ni/metal hydride (Ni/MH) batteries. The current industrial practice involves casting large ingots followed by annealing and grinding and utilizes a complex and costly alloy design. This investigation is an attempt to produce powders for battery cathode fabrication that can be used in an as-atomized condition without annealing or grinding. Both Ar and He atomization gas were tried to investigate rapid solidification effects. Sn alloy additions were tested to promote subambient pressure absorption/desorption of hydrogen at ambient temperature. The resulting fine, spherical powders were subject to microstructural analysis, hydrogen gas cycling, and annealing experiments to evaluate suitability for Ni/MH battery applications. The results demonstrate that a brief anneal is required to homogenize the as-solidified microstructure of both Ar and He atomized powders and to achieve a suitable hydrogen absorption behavior. The Sn addition also appears to suppress cracking during hydrogen gas phase cycling in particles smaller than about $25\mu\text{m}$. These results suggest that direct powder processing of a $\text{LaNi}_{5-x}\text{Sn}_x$ alloy has potential application in rechargeable Ni/MH batteries.

INTRODUCTION

Nickel/metal hydride (Ni/MH) rechargeable batteries, especially small, sealed battery packs for consumer electronics, electrical power tools and appliances are steadily replacing Ni/Cd batteries because of their extended cycling life, absence of memory effects, enhanced energy storage capacity, and reduced environmental hazard. Recent research has focused also on replacement of Pb/acid automotive batteries with large, sealed cell Ni/MH batteries for all of the above reasons, as well as a weight reduction of at least 25% for double the storage capacity [1]. However, rapid growth in Ni/MH battery applications is hampered by the need for significant improvements in battery electrode material design, processing, and cell fabrication technologies to boost Ni/MH cell performance at extended cycling lifetimes and to reduce cell manufacturing cost, which depends critically on consistent high quality metal hydride particulate.

Negative electrodes in Ni/MH rechargeable batteries could be improved significantly if fabricated from metal alloy particulate, which conforms to a following requirements: 1) large hydrogen storage capacity; 2) full capacity hydrogen absorption-desorption between -25°C and $+50^\circ\text{C}$ below ambient pressure; 3) large initial surface area; 4) fracture resistance during battery cycling; 5) chemical stability in basic solutions; 6) suitability for high volume production; and 7) low cost. The scientific and patent literature contains an extensive number of reports regarding different aspects of the crystal chemistry and hydrogen storage properties of numerous materials, concluding that rare earth intermetallic alloys [2] are preferred for cathode fabrication. However, Ni/MH battery technology is still lacking basic knowledge of how to enhance electrode performance and lower processing complexity utilizing advanced processing methods with the existing hydrogen storage alloys. Perhaps more importantly, basic knowledge is lacking on design of improved hydrogen storage alloys with optimum performance and extended cycling

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stability, based on new, less complicated and more affordable compositions that are adaptable to improvements in processing and high volume manufacturing.

Both AB₅ (LaNi₅ prototype) and AB₂ (TiNi₂ prototype) alloy compounds have been investigated for Ni/MH battery cathode material applications. Both alloys have about the same average hydrogen storage capacity of about 1.5% by weight, with the AB₂ alloys having a slightly larger theoretical maximum hydrogen storage capacity, 2.0 wt.%, compared to 1.6 wt.% for AB₅ alloys. However, to exploit the greater capacity (by weight) of the AB₂ alloys in an actual application would require a Ni/MH battery of a larger physical size, not desirable, for example, in a compact electric vehicle. This paradox arises because of the higher density for AB₅ alloys, about 8-8.5g/cm³, compared to alloys of the AB₂ alloy type, about 5-7g/cm³. Thus, a similar size Ni/MH battery of either AB₅ or AB₂ would have a similar storage capacity.

With such similar potential for practical battery application, the decision as to which compound type to pursue in this study for alloy simplification and reduction in processing complexity was determined from physical metallurgy principles. Commercial AB₅ and AB₂ alloys are quite complex, typically containing 5 to 9 elements, and both utilize some relatively expensive elements, especially Co. However, from a processing perspective, the microstructure that has been established as optimum for AB₅ cathode material performance is a homogenous, equilibrium phase [2]; compared to the optimum microstructure for AB₂ which is a highly disordered multiphase mixture of amorphous and crystalline regions [3]. For this study AB₅ alloys were chosen, because of the potential for development of a simplified processing approach without need for precise control of a metastable microstructure decomposition reaction.

The standard route for manufacturing the AB₅ battery materials includes the following initial steps: 1) melting and chill casting of large ingots; 2) extensive heat treatment of the ingots to eliminate microscopic compositional inhomogeneities, and; 3) grinding of the annealed ingots into fine powders, which may include hydriding and dehydriding to fracture large ingots into smaller pieces. Rapid solidification processing (RSP) of LaNi₅ powders by high pressure gas atomization (HPGA) has been suggested [4] as a means to suppress the Ni segregation effect observed during conventional chill casting of LaNi₅. If fully successful, HPGA could produce useful AB₅ powders directly, eliminating the homogenization anneal and the grinding steps. In other words, one of the key barriers to widespread commercialization of Ni/MH batteries for vehicle applications [1], processing cost, could be attacked by the ability to combine the above mentioned 3 steps of cathode particulate fabrication into one step by the HPGA approach.

This paper will focus on the results of our HPGA processing research on a simple AB₅ alloy, LaNi_{5-x}Sn_x, where Sn can substitutionally alloy for the Ni [5]. From previous work [5] on annealed ingot samples, the Sn substitutional addition is known to retain much of the excellent capacity for hydrogen storage of LaNi₅ (6 H-atoms per LaNi₅ formula unit) while lowering the H₂ absorption/desorption equilibrium pressure below atmospheric, practical for vehicle battery applications. Two levels of the Sn addition were tried in this study to reduce the H₂ absorption pressure and two atomization gases, Ar and He, were tried to test the influence of the external cooling rate on the rapid solidification effect in these alloys.

EXPERIMENT

The two alloys, LaNi_{4.75}Sn_{0.25} and LaNi_{4.85}Sn_{0.15}, were selected based on their H₂ absorption pressure isotherms in fully homogenized alloy particles [5]. The latter alloy produced a slightly subambient absorption isotherm at ambient temperature of about 0.9 atm and the higher Sn level suppressed the isotherm to about 0.5 atm [5]. Alloy components had purity levels of at least 99.9% for La, 99.994% for Ni, and 99.99% for Sn. The alloys were prepared as a bottom poured chill cast ingots using a high purity Al₂O₃ crucible and a pouring temperature of 1550°C.

A high pressure gas atomization (HPGA) process [4] was used to produce powders of the cast ingot of each alloy. Argon gas (99.98% purity) was supplied at a pressure of 7.6Mpa (1100 psi) to the HPGA nozzle to atomize the LaNi_{4.75}Sn_{0.25} melt, poured at a temperature of 1630°C

from an Al_2O_3 crucible. Helium gas (99.98% purity) was supplied at a pressure of 5.5Mpa (800 psi) to the HPGA nozzle to atomize the $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ melt, poured at a temperature of 1750°C from an Al_2O_3 crucible. A passivating surface film [4] was formed on the particles by injection of reaction gases at an intermediate point during atomized spray freefall within the spray chamber. Each powder yield was screened in ambient atmosphere with wire mesh sieves into size classes of dia. $< 25\text{ }\mu\text{m}$, $25\text{ }\mu\text{m}$ to $38\text{ }\mu\text{m}$, and $38\text{ }\mu\text{m}$ to $55\text{ }\mu\text{m}$ for further analysis. Some of the dia. $< 25\text{ }\mu\text{m}$ powder from each powder batch was sonic-sifted with an electro-formed Ni foil sieve in an inert atmosphere to produce a dia. $< 10\text{ }\mu\text{m}$ sample. The particle size distribution of each powder batch was analyzed with an automated laser light scattering instrument.

Chemical composition of cast ingot and powder samples were analyzed for La, Ni, and Sn by inductively coupled plasma-atomic emission spectroscopy and by inert gas fusion for C, O, and N. X-ray diffraction (XRD) measurements with Cu-K_α radiation were performed in as-atomized and annealed powder samples. Following metallographic preparation of powder cross-section samples, SEM was used to examine the solidification microstructure of as-atomized powders as a function of size class. Electron microprobe analysis provided semi-quantitative analysis of solidification segregation in powder cross-section samples following calibration with a well annealed cast sample of the initial alloy. The H_2 absorption-desorption data were obtained on as-atomized and annealed powders with an all-metal Sieverts' gas-volumetric apparatus.

RESULTS

Several previous publications of our investigations [4,6,7] have reported the essential characteristics of LaNi_5 -type powders produced by HPGA. The powders are generally spherical in shape [4,6], have a low oxygen content [7], e.g. 570 ppmw for dia. $< 10\text{ }\mu\text{m}$ powders of $\text{LaNi}_{4.75}\text{Sn}_{0.25}$, and have a fine cellular solidification microstructure [6,7] that results from rapid solidification. The cellular solidification microstructure of as-atomized $\text{LaNi}_{4.75}\text{Sn}_{0.25}$ powders consists of a cell interior phase that is depleted in Sn and a cell boundary phase that is enriched in Sn [7], compared to the nominal composition. Because both cell interior and cell boundary phases are different compositions of the same crystal structure, we refer to this phenomenon as "phase" segregation. In addition, we found [4] that unannealed, stoichiometric LaNi_5 powders produced by HPGA have an x-ray diffraction pattern indicating a single phase CaCu_5 -type structure. Their hydrogen absorption/desorption behavior and total hydrogen capacity in gas phase cycling experiments are identical to well-annealed LaNi_5 powders produced from a crushed ingot. These desirable hydrogen storage characteristics of HPGA powders probably are linked most closely to structural and chemical purity and minimal surface oxidation and to suppression of Ni segregation in the as-atomized powders. Our studies [6] also demonstrated that hydrogen gas phase cycling induced cracking of the unannealed, stoichiometric LaNi_5 powders in all but the finest sizes of the HPGA powders, less than about $5\text{ }\mu\text{m}$. Initial experiments on the Sn addition [6] have demonstrated a reduction in particle cracking from dilation stresses [8] during hydrogen cycling and a depression of the hydrogen absorption equilibrium pressure at ambient temperature to a suitable subambient pressure. As a direct result of this work [6] and other previous studies [5], the current investigation further explores substitutional addition of Sn to stoichiometric LaNi_5 , producing $\text{LaNi}_{5-x}\text{Sn}_x$ alloys.

The reason for choosing He as an alternative to Ar for the atomization gas is related to the well-known increase in the melt cooling rate during He gas atomization. In other words, an enhanced solidification rate due to the increased quenching capability of He atomization gas may suppress phase segregation in the HPGA powders of $\text{LaNi}_{5-x}\text{Sn}_x$ alloys. However, the first benefit that was noted from production of $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ alloy powder by use of He atomization gas was an increased yield of extremely fine powders, compared to the size distribution results from Ar-atomized $\text{LaNi}_{4.75}\text{Sn}_{0.25}$ powder. In fact, 84 wt.% of the He-atomized powder was less than $20\text{ }\mu\text{m}$ compared to the d_{84} value of $43\text{ }\mu\text{m}$ for the Ar-atomized powder. Such a high yield of fine powder is highly desirable from a rapid solidification perspective regardless of the

atomization gas choice because a high ratio of atomized droplet surface area/volume would enhance the gas quenching effect, important for RSP. Certainly, extremely fine powders also are preferred for battery electrodes because of enhanced surface area.

Figures 1a and b show typical powder particle cross-section microstructures from dia. $<10\mu\text{m}$ samples of Ar-atomized and He-atomized powders, respectively, to exhibit the as-solidified morphology. The backscattered electron images reveal the phase segregation pattern in both powders, although the pattern is less distinct in the He-atomized powder microstructure. The cell spacing is less than $1\mu\text{m}$ in both powders.

Electron microprobe studies of the particle microstructure cross-sections provided a semi-quantitative characterization of the effect of annealing on the phase segregation effect. The results in Figures 2a on an unannealed Ar-atomized $\text{LaNi}_{4.75}\text{Sn}_{0.25}$ particle show that the La content remained close to constant while the Sn and Ni content varied in an opposite manner. Microprobe results on an annealed particle of this alloy, given in Figure 2b, indicate that high temperature diffusion produced a homogeneous composition across the full particle diameter.

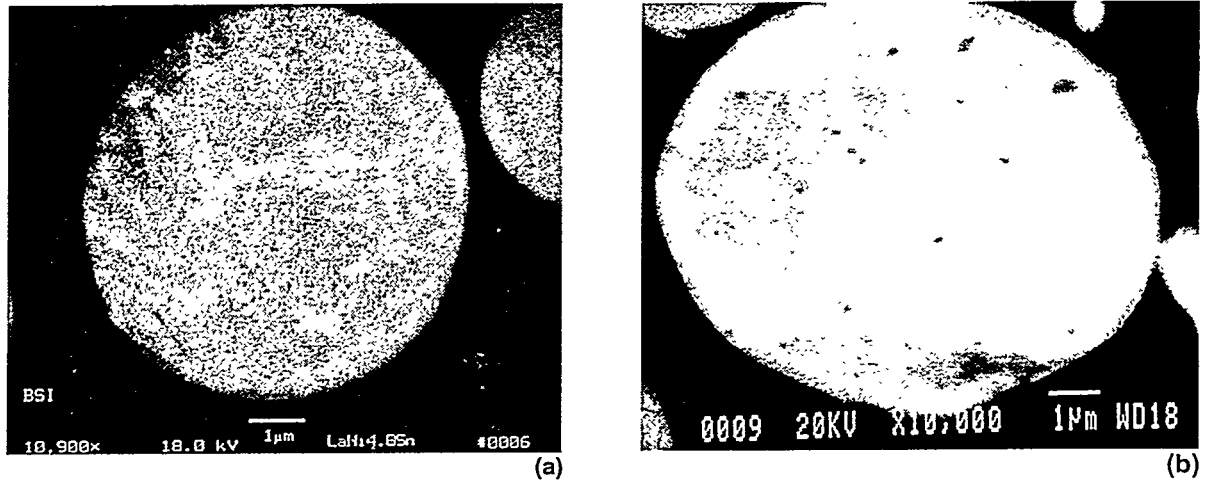


Figure 1. SEM micrographs using backscattered electron imaging of unetched cross-sections of a) Ar-atomized $\text{LaNi}_{4.75}\text{Sn}_{0.25}$ and b) He-atomized $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ showing the Sn-enriched cell boundary phase in light contrast.

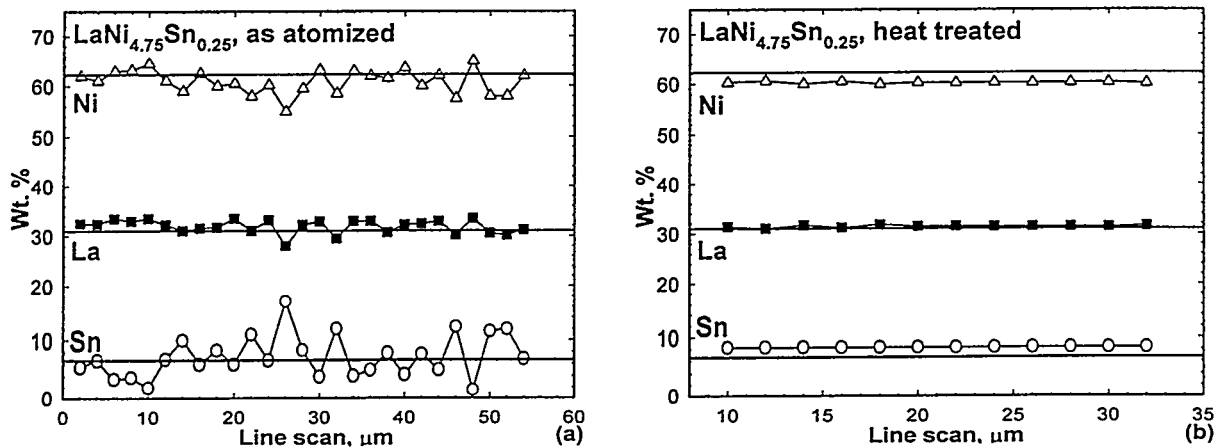


Figure 2. Comparison of electron microprobe data for a representative incremental trace across a random particle cross-section, analyzing for La, Ni, and Sn for; a) an as-atomized $\text{LaNi}_{4.75}\text{Sn}_{0.25}$ particle and b) a $\text{LaNi}_{4.75}\text{Sn}_{0.25}$ particle that was annealed at 950°C for 4 hours in vacuum.

Structural characterization of the powder by XRD was utilized to determine a minimum annealing time required for particle homogenization at an annealing temperatures greater than 900°C, as shown in Figure 3. Figure 3b reveals that a suitable compositional uniformity of the hexagonal phase was achieved in only 5 min of annealing time for the He-atomized $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ powder. The same symmetric Bragg peaks shape was achieved in 4 hours of annealing for Ar-atomized $\text{LaNi}_{4.75}\text{Sn}_{0.25}$ powder, as Figure 3a indicates.

A characterization of the H_2 gas absorption and desorption behavior of the HPGA powder is shown in Figure 4 for both of the as-atomized and annealed powder samples. The as-atomized absorption and desorption data of a 25 μm to 38 μm $\text{LaNi}_{4.75}\text{Sn}_{0.25}$ powder sample shows a sub-ambient pressure trend in Figure 4a, as desired, but has an enhanced slope compared to the ideal plateau [5] of the powder annealed for 4 hours. This suggests that the phase segregation in the solidification microstructure of the as-atomized powder provides more resistance to the transport and exchange of hydrogen, as expected. Figure 4b shows the results for He-atomized powders and illustrates that an ideal plateau-like trend was achieved by only 5 min of annealing at 900°C, consistent with the XRD data of Figure 3b that indicates phase homogenization was achieved by this rapid anneal.

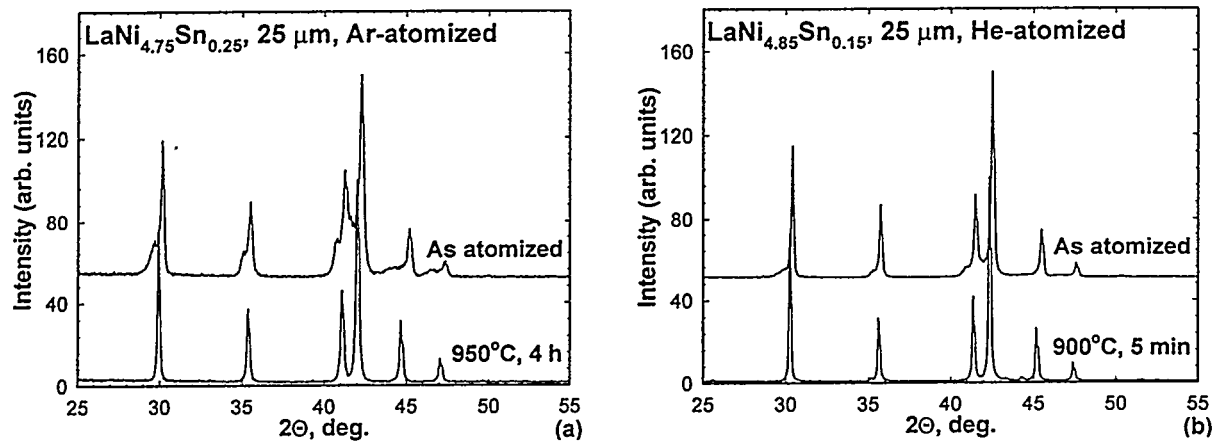


Figure 3. Comparison of XRD patterns of as-atomized alloy powder to annealed powder from HPGA powders with dia. < 25 μm of a) Ar-atomized $\text{LaNi}_{4.75}\text{Sn}_{0.25}$ and b) He-atomized $\text{LaNi}_{4.85}\text{Sn}_{0.15}$.

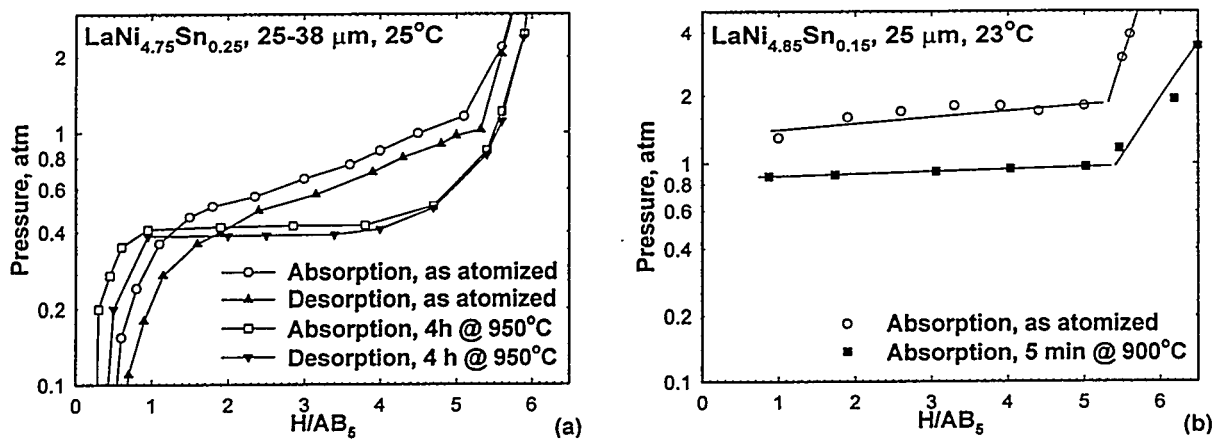


Figure 4. Summary of the hydrogen exchange behavior at ambient temperatures in as-atomized and annealed powder samples of a) Ar-atomized $\text{LaNi}_{4.75}\text{Sn}_{0.25}$ and b) He-atomized $\text{LaNi}_{4.85}\text{Sn}_{0.15}$.

CONCLUSIONS

The results of this investigation build on the previous studies [4,6,7] indicate that a high pressure gas atomization approach can produce high quality AB₅ powders for Ni/MH battery applications. A change from Ar to He atomization gas resulted in a very desirable increase in yield of ultrafine (dia. < 20 μ m) spherical powders, although complete suppression of phase segregation in these LaNi_{5-x}Sn_x alloy powders was not achieved in spite of the enhanced heat transfer coefficient of the He. The penalty in hydrogen absorption behavior of the phase segregated microstructure in the as-atomized powders was completely erased by a very brief anneal at high temperature. A good possibility exists that such an anneal could be incorporated in the atomization process sequence before removal of the powder from the unit to maintain process simplicity. Future work will involve some additional alloy composition adjustments and further modification of the HPGA process, including design of an in-situ passivation treatment for the gas atomized powder that would both minimize corrosion and enhance activation, guided by extensive electrochemical cycling experiments.

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REFERENCES

1. Anonymous, "Bridging the R&D and Commercialization Gap," Winter 1996 Newsletter, United States Automotive Battery Consortium (USABC), Troy, MI.
2. T. Sakai, M. Matsuoka, and C. Iwakura, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K.A. Gschneider, Jr. and L. Eyring (Elsevier Science B.V., 1995) v.21, p.133.
3. S. R. Ovshinsky and M.A. Fetcenko, U. S. Patent No. 5 277 999 (January 11, 1994).
4. I.E. Anderson, M.G. Osborne and T.W. Ellis, JOM, **48** (3), 38 (1996).
5. S. Luo, W. Luo, J.D. Clewley, T.B. Flanagan, and L.A. Wade, J. Alloys Comp. **231**, 467 (1995).
6. R. C. Bowman, Jr., C. K. Witham, B. Fultz, B. V. Ratnakumar, T. W. Ellis, and I. E. Anderson, J. Alloys Comp., **253-254**, 613 (1997).
7. E. Anderson, J. Ting, V. K. Pecharsky, C. Witham, and R. C. Bowman, in *Advances in Powder Metallurgy & Particulate Materials-1997*, edited by R. A. McKotch and R. Webb (MPIF, Princeton, NJ, 1997), Part 5, p.31.
8. S. B. Biner, J. Mater. Sci. (to be published).