NANOFOIL HEATING ELEMENTS FOR THERMAL BATTERIES

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Abstract

Nano-layered Al-Ni bimetallic foils are materials capable of self-propagation with either an external thermal or electrical stimuli. A study was performed to investigate the feasibility of using these materials as an alternative heat source for thermal batteries. Properties studied were flame front propagation velocity (both in absolute terms and in relation to that in the heat paper), ignitibility, heat of reaction, and electrical resistance. Additionally, two-cell and four-cell prototype batteries were fabricated with these materials and their performance was evaluated.

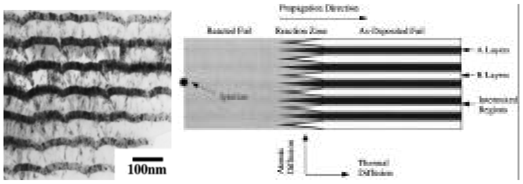
Introduction

Thermal batteries are solid state batteries used to power munitions, guided missiles, nuclear weapons, and other military systems. Depending on their design they can provide power for very short periods of time (several seconds) or can provide power for longer periods of time (minutes). Thermal batteries are composed of an electrolyte, cathode, anode, and heat pellet. Prior to activation, the battery electrolyte is in solid state but becomes molten when activated.

One issue with conventional thermal battery is the use of powdered iron and potassium perchlorate ($Fe/KClO_4$) heat pellets. For the past 20 years, $Fe/KClO_4$ pellets have been the used to heat thermal batteries. When the heat pellet reacts it generates heat to melt the electrolyte thus generating current in the battery. With the advent of advanced munitions technologies, the need for non-cylindrical batteries is becoming critical. It is extremely difficult and expensive to produce non-cylindrical $Fe/KClO_4$ pellets. These pellets are prone to static discharge, friction sensitivity, and are very brittle. Additionally, the DOD's initiatives to remove perchlorates from military munitions gives further impetus in finding alternatives to perchlorate based heat pellets.

One potential alternative to pyrotechnic heat pellets are reactive nano materials that give off heat upon initiation. These reactive materials are non-pyrotechnic and do not suffer from the same problems as the $Fe/KClO_4$ pellets. In this study we evaluated the use of commercially available Ni-Al foils from Reactive NanoTechnologies as a replacement heat source.

NanoFoil is a trade name given by Reactive NanoTechnologies (RNT) to a class of foil materials made from alternating layers of Ni and Al only a few dozen nanometers thick. By making the alternating layers nanometers-thin the NanoFoil can support a self-sustained reaction front once it is initiated. The reaction could be set-off by spark, current pulse, mechanical shock, or anything that would create a local hot spot. Figure 1 is a high resolution edge-view image of an Al-Ni NanoFoil (a) and a self-propagating reaction in such a foil (b). In this paper, the Nanofoil refers to Ni-Al foils that react to form NiAl and heat.



(a) (b)

Figure 1. (a) An edge-view by TEM of a NanoFoil with alternating layers of Al (brighter) and Ni (darker) (1). (b)

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Speed of the Exothermic Reaction

The speed of the exothermic reaction in the NanoFoil was measured by photographing the flame front with a high speed camera[1]. Figure 2 shows the progression of the flame front in a 2.54 cm long by 100 um thick foil. In this measurement the foil was initiated with Nichrome wire (shown at t=0)[2]. Based on the flame front position and time the flame front velocity is approximately 9 m/s. To put this in perspective, the flame front travels 2.54 cm in approximately 3 ms. A summary of the speeds measured for several different NanoFoils is given in Table 1.

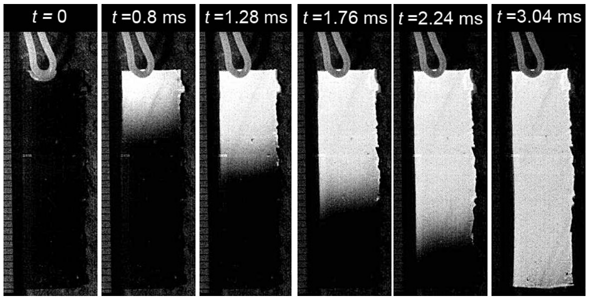

Figure 2. Photos of flame front progression in NanoFoil strip by a high speed camera. $t = 0$ is when the initiating current was passed through the clip.

Foil thickness / ? m	Average speed / $m\,s^{-1}$	Standard deviation / $m\,s^{-1}$
150	7.61	0.17
100	8.97	0.24
80	7.59	0.34
60	7.52	0.27

Table 1. Speed of the exothermic reaction in NanoFoil as measured by flame front propagation.

Another experiment performed was to place a NanoFoil strip vertically on a piece of heat paper and ignite the heat paper on the far end with a nichrome wire (Figure 3). This was to observe the ease with which a NanoFoil disc could be initiated edgewise by a heat paper fuse strip. As can be seen, the heat paper initiated the NanoFoil strip. The flame front in the NanoFoil was much faster than the heat paper.

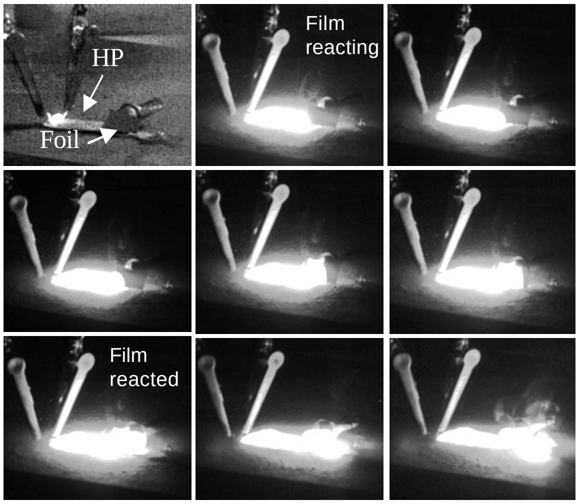

Figure 3. High speed photos of a vertical NanoFoil strip being ignited by the underlying heat paper. In the first picture in the upper left of the sequence the nanofoil is designated by foil and the heat paper is designated by HP.

Heat of Reaction and Electrical Resistance

The heat of reaction for 100 ? m and 150 ? m NanoFoils were measured at 239.8 cal/g and 242.8 cal/g, respectively. These values are slightly higher than that of $Fe/KClO_4$ heat pellets.

Electrical resistance of the NanoFoil increased somewhat after reaction, although the precise measurement was difficult due to the curling and buckling of the post reacted foils. The best value obtained was 5 m? for 0.5 to 1-inch reacted segments, measured with a 4-point Kelvin probe and an Agilent 34401A multimeter.

Control of Peak Temperatures with Buffer Discs

As stated previously, the Nanofoil materials have extremely fast flame front velocities, resulting in fast temperature rise. This can result in overheating the cathode and anode materials adjacent to these heat discs. One way of limiting the peak temperature that the neighboring pellets experience is to place stainless steel discs on both sides of the NanoFoil discs as thermal buffers. For this series of experiments, we used 100 ? m-thick NanoFoil Discs and 76 ? m-thick 304 stainless steel discs, both with a diameter of 1.9 cm. Different combinations of the NanoFoil and buffer discs were tested, with an experimental setup depicted in Figure 4. Figure 5 shows the temperature-time curves recorded for many such combinations, from which peak temperatures can be determined.

When these peak temperatures are plotted as a function of both the numbers of NanoFoil and buffer discs, a clear trend emerges from the resulting 3D plot (Figure 6). As expected, the peak temperature increases with the number of NanoFoil discs and decreases with the number of buffer discs. It was also observed that the peak temperature declined faster with increasing number of buffer discs than

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[1] Vision Research Phantom V7.1 at 6250 frames per second.

[2] Passing a current through thin Nichrome wire raises it temperature to over 1000°C.

reducing the number of foil discs. Thus the peak temperature can be controlled either by increasing the number of buffer discs, reducing the number of reactive foils, or by some combination of both. Figure 6 also shows that at least two buffer discs are required to limit the peak temperature to 600 °C. This is critical to avoid melting the anode and cathode.

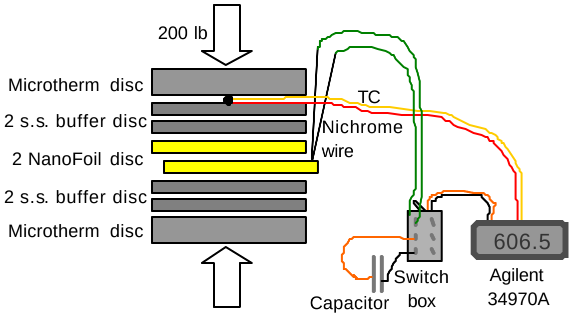

Figure 4. Experimental setup for the determination of peak temperature on the outer surface of the buffer discs sandwiching NanoFoil discs. The foils are initiated and the attached thermocouples measure the temperature rise of the stack. The microtherm discs are used to limit the axial heat transfer from the stack.

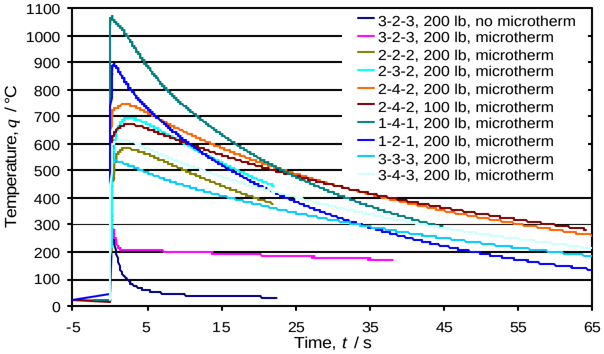

Figure 5. Temperature-time curves obtained in the peak temperature experiments for different combinations of NanoFoil and buffer discs.

Flow of a Reacting NanoFoil under Pressure

The NanoFoil discs were observed to flow after reaction when compressively loaded. Figure 7 shows the photos of three as-reacted buffer discs-foil stacks. The three NanoFoil disc stacks were sandwiched by two buffer discs. As can be seen, the 4foil stack compressively loaded with 200 lbs released the most material while the stack with 2 foils released the least amount. It appears that the amount of material released is influenced more by the amount of NanoFoil material being compressed than by the applied compressive load. This is not surprising since more NanoFoil discs in a stack would result in a higher temperature in the stack, therefore generating more molten material. Knowing that aluminum melts at 660 °C and the local temperature in the stack can easily rise above 1000 °C (see Figures 5 and 6), one would expect to see such material flows.

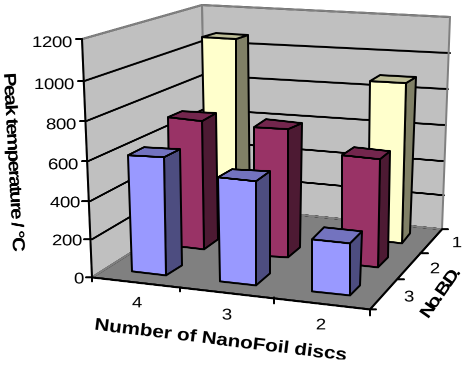

Figure 6. Peak temperatures on the outer surfaces of the buffer-Nanofoil-buffer sandwich stacks of different combinations, plotted as a function of both the numbers of the NanoFoil and buffer discs (BD).

Another possibility for this flow behavior is the presence of a low melting braze on the foils. The foils in this study were coated with a 5 ? m layer of braze on both sides of the foils. When the foils are initiated, the braze melts enhancing the contact between the surfaces to be joined. If one envisions a multilayer stack of compressively loaded foils, the molten braze may allow the layers to slide by one another, thus causing some of the foils to extrude from the stack. This undesirable behavior of the NanoFoil could be a severe hurdle to its application to thermal battery, at least for the current pellet construction. The material would seep along the sides of the cell stack and short out the thermal cells (Figure 8).

The pressure on a buffer-NanoFoil-buffer stack under test was observed to drop significantly after initiation. For example, the applied pressure in a 2-cell battery dropped from 100 lbs to zero pounds after initiation. Recent experiments performed with a 2-3-2 (stainless steel disc-nanofoil disc-stainless steel disc) minimally brazed foils (100Å thick) showed a reduced pressure drop upon initiation. For foils loaded to 100 lbs pressure, there was no pressure drop. For a 2-4-2 configuration loaded to 200 lbs the pressures dropped to 150 lbs upon initiation. Material was still extruded from the sides of the stack.

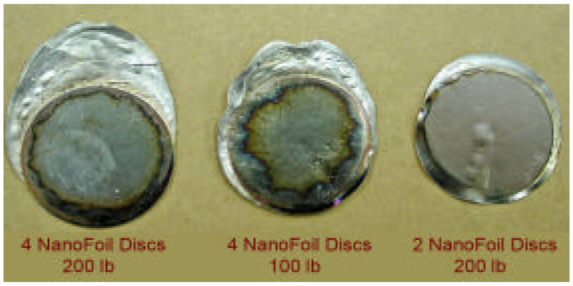

Figure 7. A photo of some reacted buffer-NanoFoil-buffer sandwich stacks, demonstrating different hot-flow behaviors under different conditions

Figure 8. A photo of a reacted buffer-NanoFoil-buffer stack still on the press, demonstrating the liquid-like behavior of NanoFoil material

NanoFoil-Heated 2-Cell Batteries

The first NanoFoil-heated battery was a 2-cell stack, as depicted in Figure 9. As the battery was under-heated and under-insulated, it was discharged with the 200mA current. The results, as plotted in Figure 10, demonstrate a well-performing battery carrying the load for 112 seconds (cutoff voltage 0.2 V). The temperatures on its top and bottom electrodes give almost identical traces, and never exceeded 600°C, consistent with the previous observations. Based on the LCCM benchmark of 90-s runtime at a discharge current of 1.5 A, this battery delivered only 17% of the total electrochemical capacity[3]. It was therefore severely temperature-limited: at cutoff, its electrode temperatures (360 °C) were already substantially below the eutectic point of 435 °C

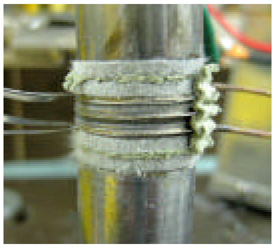

Figure 9. Photo of a NanoFoil-heated 2-cell thermal battery before initiation, corresponding to the schematic drawing of Figure 1

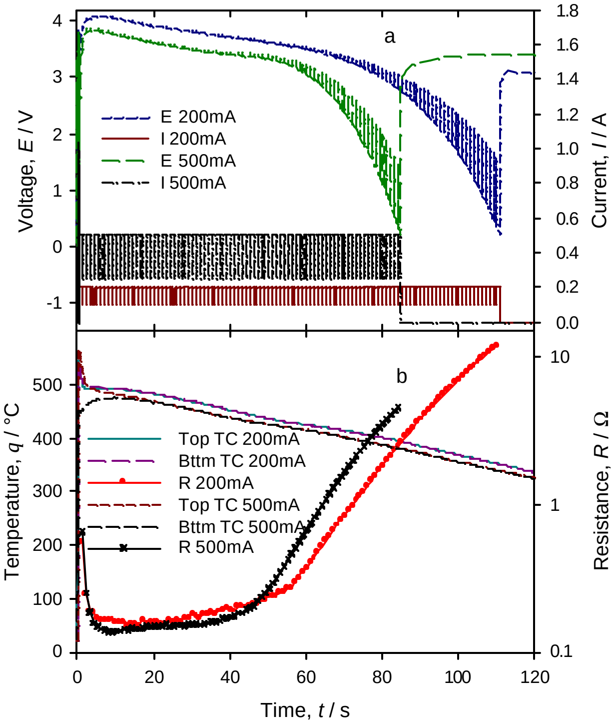

Figure 10. Profiles of voltage (a), current (a), temperature (b), and resistance (b) for two NanoFoil-heated 2-cell batteries discharged at 200mA and 500mA currents.

Encouraged by the results of the first battery, another battery identical to the first one was constructed and discharged at 500mA current. The results are plotted in Figure 11 together with those of the first. This time, the battery ran for 84 seconds, only 25% shorter than the first, with a discharge current 2.5 times as large, drawing 31% of the total capacity. These values further confirm that the discharge of the first battery was limited by temperature, as well as of this one. The voltage plateau, as shown in (a), is lower than that of the first by about 0.35 V, caused primarily by the more severe polarizations (such as concentration polarization) under the heavier discharge current. The resistance calculated from the current pulse and voltage response, however, is almost the same, demonstrating that the processes causing the plateau shift are indeed slow processes. As shown in (b), the electrode temperatures at cutoff were about 380°C, 55° below the eutectic point.

A Pyrotechnic-Heated 2-Cell Battery

In order to directly compare the properties of NanoFoil discs in the thermal battery with those of pyrotechnic heat pellets, another 2-cell battery was built using three pressed Fe/$KClO_4$ pellets in the places of the three 2-3-2 (stainless steel disc-nanofoil-stainless steel disc) NanoFoil stacks. It was discharged at 500mA, with the results plotted in Figure 11. As can be seen from the initial disturbances in the voltage profile and particularly in the

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[3] LCCM is a pellet based thermal battery developed at ARL several years ago.

temperature profiles, the bottom heat pellet failed to ignite until 7

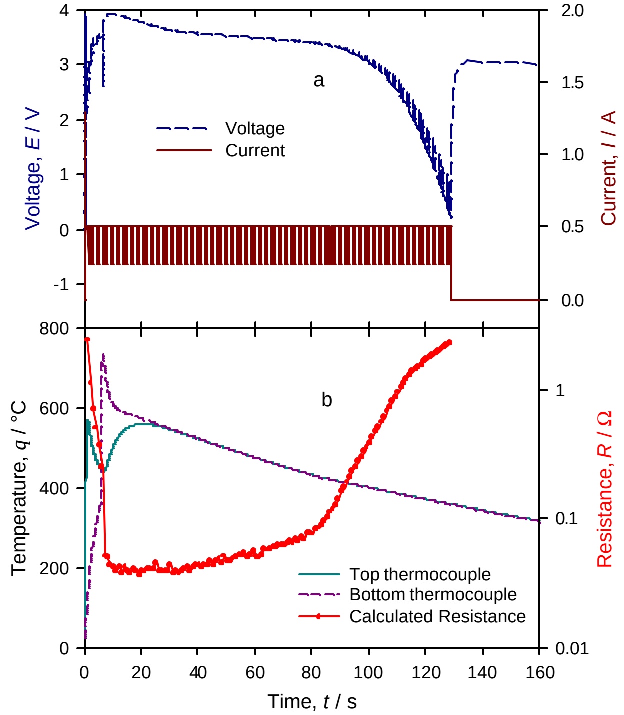

Figure 11. Profiles of voltage (a), current (a), temperature (b), and resistance (b) for an Fe/$KClO_4$ pellet-heated 2-cell battery discharged at 500mA current.

seconds into the discharge when it was initiated by the heat from its neighboring components. The battery performed normally for 128 seconds until cutoff, drawing 47% of the total capacity. But it was still temperature limited, and its electrode temperatures were 370 °C at the cutoff, 65° below the eutectic point, as can be seen in Figure 11 (b).

A NanoFoil-Heated 4-Cell Battery

Based on the success of the two cell thermal battery, a nanofoil heated 4-cell battery was built and discharged at 500mA current. Figure 12 shows photos of the 4cell battery both before and after its initiation, and Figure 13 shows the different profiles as the results of its discharge. At initiation, the pressure applied on the stack dropped from 100 lb to almost 0, likely due to the extrusion of reacting NanoFoil material, shown visually in the photos of Figure 12. Drop of pressure at initiation have been observed for all the NanoFoil-heated batteries, but it was particularly severe with the 4-cell battery.

Similar pressure drop in the pyrotechnic pellet-heated battery was much milder; it was observed to drop from 100 lb to 40 lb at its initiation. As marked by the vertical dashed line in Figure 13, at about 6 seconds into the discharge, the pressure on the stack was manually restored back to 100 lb. This pressure increase lowered internal resistance from 1.3 to 0.6 ? and thereby raised the voltage plateau by about 0.35 V (=0.7? ? 0.5A). About 25 seconds into the discharge, the pressure was increased again, as marked in Figure 13 (b), but this time the effect was minimal. Overall, the 4-cell battery performed reasonably well, discharging to 0.4 V for 74 seconds with a discharge of 27% of the total capacity. At its cutoff, both of its electrodes were at the temperature of 380°C, 55° below the eutectic point.

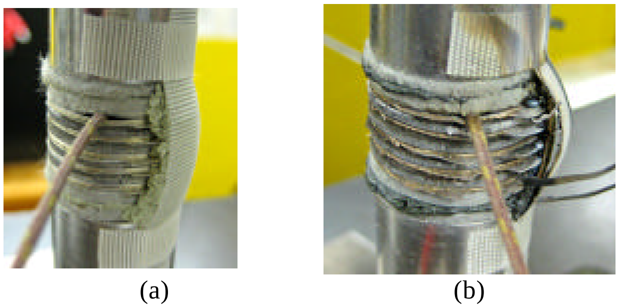
(a) (b)

Figure 12. Before (a) and post-initiation (b) picture of the four cell thermal battery.

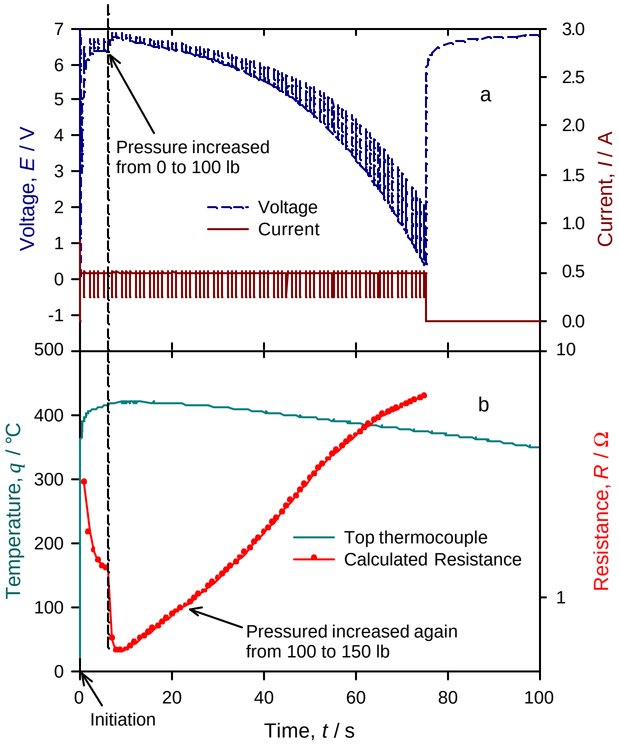

Figure 13. Profiles of voltage (a), current (a), temperature (b), and resistance (b) for a Nanofoil 4-cell battery discharged at 500mA current

Conclusions

NanoFoil materials have many favorable traits for use as a heat source in thermal batteries. It had a slightly higher specific heat of reaction than pyrotechnic heat pellets. The flame front velocity of 9 m/s is considerably faster than heat paper. Flame from heat paper is hot enough to ignite Ni-Al NanoFoil strips. The Ni-Al foils are electrically conductive both before and after initiation.

When compared to the pyrotechnic heat pellet, the NanoFoil generates a significantly steeper temperature rise than pyrotechnic pellets. The rise in temperature can be reduced by bounding the foil stacks with stainless steel buffer discs. The temperature on the outer buffer discs was found to depend more on the number of buffer layers than on the number of NanoFoil discs.

Two issues exist with implementing NanoFoil in thermal batteries. Upon initiation, the foils tend to flow under pressure which could lead to electrical shorting of the battery. The second issue is the drop in applied load upon initiation, which leads to an increase in the battery internal resistance.

Acknowledgement

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