WOLAA LEAF

Winter 2006
Volume VIII, Issue I

WOL Oral History Supplement

NITINOL Re-Examination

By
William J. Buehler

WOLAA Web Site: www.wolaa.org

I have noticed with great pleasure the rather frequent reports in THE LEAF on NITINOL and its varied applications. The summer issue (Vol. VII, Issue III) emphasizes an overlooked point. That being the RECOGNITION of the inventors, NOL and U.S. Navy in the discovery and early development of NITINOL.

The RECOGNITION aspect along with the frequent misleading reference to its "ACCIDENTAL DISCOVERY" are the two sensitive areas that need some clarification. Since I initiated the NITINOL research during the summer of 1958, I feel compelled and qualified to address these two subject areas. Please allow me, as concisely as possible, to shed some early historical light on those two emotionally delicate areas.

DISCOVERY

Let me first address the issue of what I feel to be "DISCOVERY" rather than what is too frequently described as "ACCIDENTAL DISCOVERY." In order to differentiate between the two views, let us examine a condensed version of the key points of conception, research and early development. These are chronologically provided as follows:

Problem (1958): To find a metallic alloy material to withstand the high temperature rigors of a missile re-entry nose cone.

Concept: I chose to investigate metallic alloys that formed intermediate phases, of the intermetallic compound type, particularly those that tended to exhibit melting temperatures higher than the alloying component metals.

Literature Search: During the summer of 1958, I spent about one week at the Library of Congress. While there, I primarily searched through Max Hansen's lengthy text, Constitution of Binary Alloys (1958), for intermetallic compound alloys that met my predetermined criteria. Around sixty compound systems were selected. These were, for numerous reasons, reduced to twelve compound systems. The equiatomic nickel-titanium (basic NITINOL) was one of the twelve selected for further study.

Hand-on Study: With a support staff attrited to two sub-professionals (Messrs. Edward Everly and Ernest Heintzelman), I employed the simplest and most direct techniques to become more familiar with the selected twelve systems and a few of their overt properties. The twelve systems were alloyed by controlled-atmosphere arc-melting into cast button form (approximately 1/2" thick by 2 ½" diameter). Their relative brittleness was determined by the simplest and most crude test of striking the cast buttons with a hammer. The twelve varied from being highly brittle (ionic atomic bonding) to highly impact resistant (metallic atomic bonding). Equiatomic nickel-titanium (basic NITINOL) was the most impact resistant and invited further study. Wrought forms of this alloy were produced. This was accomplished by hot and cold rolling, hot and cold swaging and wire drawing at room temperature.

Startling Discovery: Arc cast bars (approximately 5/8" diameter by 4" long) when suspended and struck rang brilliantly when heated slightly above room temperature. The same bars were leaden-like when cooled slightly and struck. VOILA! The equiatomic nickel-titanium was acoustically signaling that it was quite unusual and unique. This equiatomic nickel-titanium compound alloy system seemed, at the time, to be almost "crying-out" for more thorough investigation. More detailed quantitative metallurgical research was undertaken.

Shape Memory: The above acoustic damping as a function of temperature was truly startling. This overt property change was immediately felt to be related to some change at the atomic or crystalline level. Messrs. Raymond Wiley and David Goldstein, both Metallurgists, joined my group and assisted greatly with the multitude of early physical, mechanical and metallographic studies.

Simultaneously, Dr. Frederick Wang also joined my enlarging group. Dr. Wang's interest and expertise in basic atomic crystal physics was vitally needed. He immediately undertook the research into the basic understanding of these unique alloys, at the atomic level, which included by then the "shape memory" as well as the acoustic damping change as a function of composition and temperature. Before his arrival, the various unusual and unique behavior was analogous to having a "black box" that overtly performed—but we lacked the most rudimentary basic understanding of why and how.

Let me digress here slightly and describe the "shape memory" finding. Some very early overt indications of it occurrence were:

*Cold rolled sheet and cold drawn wire, when heated (annealed), noticeably reduced in length.

*Hardness measurements (indentations), made at room temperature, markedly reduced in size with heating to moderate temperatures.

*The acoustic damping change with modest temperature change occurred roughly at about the same temperature range as the above observed shape changes.

*Metallography revealed, under certain conditions, an acicular microstructure that is characteristic to metallurgists of a Martensite structure. This structure was particularly noted to be related to the stressing of the specimen's surface during metallographic specimen polishing. More careful stress-free polishing was found to avoid its formation.

The above indications of some "shape memory" behavior, while perceived, were somehow still not sufficient to sense the very major shape recovery possible in these alloys at near room temperature. That large and unique "shape memory" was found, of all places, at an NOL management meeting. For that meeting, I bent a thin-strip of NITINOL into an accordion shape. It was intended to be flexed numerously to demonstrate the material's fatigue resistance. Dr. David Muzzey, Associate Director, applied heat from his pipe lighter toe collapsed strip. The strip immediately extended with considerable force. VOILA! VOILA! A truly unique "shape Memory" alloy with significant magnitude of force and with significant energy conversion (heat energy ➔ mechanical energy) was revealed. Our earlier above findings were trying to tell us something but the bend ➔ heat ➔ recovery of such gross magnitude was a truly astounding finding. Who said management meetings are a waste of time?

Crystallography and Property Data: At this point in time (approximately 1962), we had uncovered a truly unique metallic alloy material. We had to now understand its basic atomic behavior and characterize its many properties to make it reliable for possible product use. It was here that Dr. Wang accepted the basic atomic level challenge and soon through appropriate selective research provided conclusive basic understanding of the very complicated Martensitic transition responsible for NITINOL's unique overt properties.

Technology Transfer: Awareness of NITINOL's unique combination of properties quickly radiated outside NOL. This occurred mainly through technical reports, presentations, various forms of media coverage and NOL's Technical Information Organization. Let me cite just a few examples of the key organizations that became involved. NASA independently sponsored two major characterization studies, one at Battelle Memorial Institute (under Dr. Curt Jackson) and a second at Goodyear Aerospace Corporation (under William Cross). Dr. George Andreason, DDS, Professor at the University of Iowa, using some variable composition NITINOL wires, started studying its use as an orthodontic bridge (arch) wire. Raychem Corporation (under Jack Harrison) independently developed the successful hydraulic couplers for the then new U.S. Navy's F-14 jet aircraft. These very low transition temperature ternary alloy couplers were expanded radially in liquid nitrogen and then, on warming to room temperature, radially contracted with great force coupling the connecting pipes. The coupler was Trade Marked "Cryofit™." Raychem also developed an electronic connector called

"Cryocon™."

These were some of the early technical accomplishments during the super active and harried 1960's. Following these lines of activity, the medical people were starting to show some interest. That initial interest was primarily under Lt.Col. C. A. Heisterkamp, MD., at Walter Reed and Dr. James Hughes, MD., an orthopedic surgeon at Johns Hopkins. This early medical research activity ultimately led to the many very important special medical devices employed today.

I could continue endlessly recalling detail from memory. But my main objective is to convince the readers of THE LEAF that NITINOL was a rather planned DISCOVERY and not an ACCIDENTAL DISCOVERY.

An "Accident" by definition implies some occurrence that is unplanned, unintended, without forethought, etc. Above, I have tried to describe the intentional step-step forethought and designed research that stimulated the initial finding, development and technology transfer that made NITINOL into a very unique, new class of metallic material.

Conversely, I will accept the sometimes used term SERENDIPITY for NITINOL which Webster describes as "finding valuable or agreeable things not sought for." But I hope the above detail confirms my objection to NITINOL being referred to as an ACCIDENTAL DISCOVERY.

I retired from NOL in 1974, quite exhausted and as they say, "burned out." Being involved simultaneously with technical leadership, technical writing, public information, sample requests, progress reporting, meetings, etc., finally took their toll. However, I was not alone in working hard. Over the years, from the humble beginning with two sub-professional assistants, I acquired part or full-time professional and non-professional associates who also worked diligently. Most have been mentioned. However, I would be greatly remiss not to mention the great sub-professional services provided by Messrs. Charles Sutton and Richard Jones. They aided the program immensely with the preparation of metallurgical research items and very timely and important technology transfer samples.

RECOGNITION

A question raised in the Summer 2005 issue of THE LEAF: Have NOL, the inventors, and early developers gotten deserved credit? Recognition by its very nature is always a rather sensitive subject. NITINOL recognition is no exception. Allow me to relate my personal experiences in this area. Understand, my comments on this subject are solely my own and they should not be considered to necessarily express the feelings of any of my living former associates.

For some unknown reason, the NITINOL development has gotten much more of its recognition and acclaim outside the government, Navy, and the NSWC Laboratory. Let me illustrate by citing just one very typical and gratifying example. In September 1988, several years after the universal acceptance and use of NITINOL in the highly important area of dental orthodontic bridge (arch) wires, I received a letter from Dr. George Andreasen, DDS, the key researcher who first employed NITINOL for orthodontic use. Let me take out of context two very pleasing sentences from that letter. They read: "The dignity you are still receiving has spread around the world in your development of the alloy—NITINOL. ...If you would not have sent me the 3-foot piece of cobalt substituted NITINOL wire, I could not have applied it to orthodontics. In fact, I'll be in your debt forever." This example praise for cooperative technical early assistance is somewhat symbolic of "outside" recognition.

Very early, the unique properties of these alloys indicated a promising future. In order to assure that the development would always reflect favorably on NOL, I named these alloys NITINOL (Nickel-Titanium-Naval-Ordnance-Laboratory). At the beginning, there were two NITINOL compositions of interest: 55-NITINOL, 55 weight percent nickel—the "shape memory" alloy—and 60-NITINOL, 60 weight percent nickel—a non-magnetic precipitation hardenable tool-like material. With time, the "shape memory" composition became so popular that numerical values were dropped and the name NITINOL was considered to be almost exclusively the "shape memory" alloy. History has confirmed the value of this early naming as it has given the Naval Ordnance Laboratory continuing recognition.

Let me now briefly review the area of formal individual recognition. In 1961, I received the Meritorious Civilian Service Aware, a recognition that I was pleased to receive and at that time in keeping with the very early NITINOL research and development activity.

About ten years later, in 1971, after a great deal more in-house research and development, and by then far greater application in a wide diversity of products, Dr. Wang and I were jointly nominated by NOL management for a higher level Navy award. Our award was rejected. The rejection was primarily based upon, and I quote, "....not yet proven itself." The spokesperson for the rejecting committee further suggested to the NOL representative other award levels, and I quote, "....let it jell for a while, wait and see how much NITINOL is used, and then try for one of these awards."

Now let me pan ahead in time to the somewhat humorous part. As suggested in 1971, I, in 1993, thought on behalf of Dr. Wang and myself it seemed time to remind the Navy and more specifically NSWC of the earlier suggestion. Contact was made with NSWC management. Historical, technical, and application details were submitted. Nomination for any further recognition award was rejected at the NSWC level. To be brief, the primary reason for rejection, among other lesser reasons, was simply the passage of time. I quote from context from an NSWC letter dated 24 November 1993: "I struggled with evaluating the consistency of such an award with Division and Navy philosophy, policy and practices, and the significant setting of precedent that your nomination for such and award would make, i.e., thirty-five years after discovery and nearly twenty years after employment." Followed in the second paragraph: "Proposing either of these highest level Navy awards for work conduced in a Navy Laboratory many years ago would have to carry very compelling reasons for its justification at this time." End of story! Does my recollection to the CATCH-22 scenario seem to be in play here?

In an overall sense and on balance, I feel that the continuing commercial non-government recognition for NITINOL has been very favorable and highly appreciated. Most commercial products continue to use the NITINOL name. Stories by NOL/NSWC retirees like those in the summer issue of THE LEAF are deeply pleasing. Further, many current versions of the Webster Dictionary carry the NITINOL name. More importantly, they usually reference the "Naval Ordnance Laboratory," where it was created. Still further, a search of the Internet provides many references to NITINOL and its many applications.

My personal regard for recognition, and I feel quite certain also expresses the feelings of those who worked with me, requires no additional formal recognition at this time. Our satisfaction really lies in the many wonderful results being accomplished in the area of engineering, dentistry and life-saving medical applications.