Hardening behavior and phase decomposition in very Ni-rich Nitinol alloys

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ABSTRACT

A series of Ni-rich Nitinol compositions spanning from 53NiTi to 58NiTi (at%) have been solutionized at 1050 °C and aged at 400 °C, 625 °C, and 750 °C for varying times to determine the correlation between microstructure and hardenability. Compositions of 55NiT, 56NiTi, and 57NiTi displayed peak hardness values near 650 VHN upon quenching, which are on par with tool steels. Upon aging at 400 °C, all but the 55NiTi and 56NiTi compositions exhibited a decrease in hardness initiating, between 1 and 10 h for the lower Ni alloys and after 100 h for the highest Ni containing alloys. The high hardness, including the solution treated condition, was attributed to the precipitation of a large volume fraction of nanoscale Ni_4Ti_3 platelets that resulted in narrow B2 NiTi matrix channels. These channels provided a micro-structure-driven strengthening morphology. Upon increasing Ni content to greater than 56NiTi and increasing the aging time and temperature, the Ni_4Ti_3 phase decomposed to either Ni_3Ti_2 and/or Ni_3Ti with a subsequent loss in hardness. The decomposition morphology between the precipitates was characterized by serial sectioning showing that Ni_4Ti_3 platelets acted as a heterogeneous nucleation site and subsequent Ni-reservoir during the growth of globular Ni_3Ti precipitates.

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1. Introduction

The thermoelastic martensitic transformation in NiTi and its variety of off-stoichiometric compositions, commonly referred to as Nitinol, is responsible for shape memory and superelastic behaviors [1–3]. The equiatomic NiTi and Ti-rich Nitinol alloys have received significant attention, particularly for actuator based applications, because of their modestly higher shape memory transformation temperatures and larger recoverable strains than their Ni-rich counterparts. Of the Ni-rich alloys, compositions containing 50.7–52 at% Ni have been extensively studied and optimized primarily for superelastic biomedical applications such as stents, staples, vascular filters, and orthodontic arch wires [4–7]. Unfortunately, as the composition becomes increasingly Ni-rich, a precipitous drop in transformation temperatures, well below room temperature, occurs making them impractical for the majority of actuator and turbo-machinery engineering applications [1,2,8]. Consequently, the exploration of even higher Ni-rich compositions has been largely ignored.

Though very Ni-rich Nitinol alloys are impractical for many shape memory applications, Buehler et al. [9] noted that Ni contents on the order of 55 at% (60 wt%) exhibited a unique set of properties, which were stably non-magnetic and included high hardness, moderately lower density than most structural metals, and corrosion resistance even in marine environments. Subsequently Buehler proposed the use of such alloys in non-magnetic hand tools, hardened penetrators, and bearings for water flooded rotating components [10]. Despite Buehler's early observations and insights, these very Ni-rich Nitinol alloys were quickly overshadowed by their shape memory alloy counterparts and never matured.

Recently, a renewed interest in 55Ni–45Ti (at%) has emerged for bearings and other mechanical components. DellaCorte et al. and others have noted that this alloy can be lubricated, unlike Ti alloys [11–13], and it had hardness on par with tool steels. Coupling the exceptionally high hardness with a low effective modulus allows this alloy to undergo very large strains without permanent deformation. These latter traits reduce the chance of structural damage at contact points during shock loading [11,14]. Combine this with outstanding corrosion resistance, and this alloy is now being considered as a replacement for bearings in the water recycling system for the International Space Station [15]. Though

this specific Ni-rich Nitinol alloy has emerged as a promising new bearing and possible structural material, little has been done to characterize the hardening mechanisms, thermal stability of the microstructure and its effect on hardness, or how these properties change relative to other Ni-rich compositions. Without such information, it is not possible to systemically optimize alloys for future bearing applications.

Fig. 1 shows the binary phase diagram for the Ni–Ti system [16]. The stoichiometric B2 NiTi alloy is a line compound up to $\sim 625\,^\circ$C, where upon it can accommodate an increasing Ni-rich site occupancy with increasing temperature. This provides the Ni-rich alloys a B2 solutionizing phase field. Upon cooling from this single phase field, precipitation of the thermodynamic equilibrium Ni_3Ti phase is expected. Though this is the equilibrium phase, many reports have revealed the initial precipitation of metastable Ni_4Ti_3 and/or Ni_3Ti_2 phases [17–21]. In particular the rhombohedral Ni_4Ti_3 precipitate phase has been shown to be critical in stabilizing the shape memory and superelastic behaviors of moderately Ni-rich alloys [22,23]. Upon increasing temperature or extended times, these metastable phases eventually decompose to the stable Ni_3Ti phase. Nishida et al. [17] provided a summary time–temperature-transformation diagram for a 52NiTi (at%) alloy, which revealed the decomposition sequence for these various Ni-rich precipitates. As precipitation type and sequence are critical to age hardening, identifying the microstructure and aging behavior for these Ni-rich compositions is critical to understand the hardenability noted in the 55NiTi alloy. Thus, this work provides a comprehensive processing-structure-property study for Ni-rich Nitinol alloys spanning 53–58 at% Ni to reveal the underlying strengthening behavior and its evolution and thermal stability at low and intermediate aging behaviors.

2. Experimental procedures

A series of 53Ni–47Ti, 54Ni–46Ti, 56Ni–44Ti, 57Ni–43Ti, and 58Ni–42Ti (at%) alloys were fabricated as arc-melted 80 g buttons that were ~ 4 cm in diameter. Starting with the appropriate weights of high purity elemental Ni and Ti constituents, the alloys were melted. After the initial melting, the ingots were reversed and re-melted at least 4 times under a protective partial pressure of argon to increase the homogeneity of the solidified melt. Following casting, the individual buttons were further homogenized in vacuum at 1050 $^\circ$C for 24 h and furnace cooled. A 55NiTi (at%) alloy was acquired from ATI Wah Chang, Portland, Oregon to match the composition of Buehler and DellaCorte who had noted with the high hardness. In former reports [9–15] this material is referred to as 60NiTi or 60Nitinol, which is in reference to its weight percent. The as-received condition of the material was a hot-rolled plate that had been heated to $\sim 980\,^\circ$C for 150 min then oil quenched.

To ensure uniformity in all the starting processes, all alloy compositions were sectioned into smaller pieces and re-solution annealed at 1050 $^\circ$C for 10 h followed by water quenching. Subsequent aging was then conducted at 400, 625, and 750 $^\circ$C for various times. The solution treatment and water quench was found to be critical in achieving the high hardness. In contrast, furnace cooling allowed the formation of coarse stable and metastable Ni-rich precipitate phases resulting in a much lower hardness [24]. All of these solution annealing and aging processes were conducted in a tube furnace under a continuous flow of ultra-high purity Ar with the specimens wrapped in a Ta foil to reduce oxidation. For any aging conditions longer than 24 h, the specimens were wrapped in a Ta foil and encapsulated within a quartz tube backfilled with Ar to further minimize oxidation for these extended aging times.

Phase identification and microstructural characterization were performed by transmission electron microscopy (TEM), scanning electron microscopy (SEM), and X-ray diffraction (XRD). TEM samples were prepared by cutting 3 mm discs, grinding the discs to $\sim 100\,\mu$m in thickness, followed by dimpling the discs using a 6 μm diamond suspension to a final thickness $< 10\,\mu$m in a Fischione Model 200 Grinder. Once dimpled, the discs were then ion milled using a Gatan 691 Precision Ion Polishing System until electron transparent perforations occurred in the dimpled region. All specimens were analyzed in a FEI Tencai G2 F-20 Supertwin (scanning) transmission electron microscope ((S)TEM) operated at 200 keV. SEM specimens were polished with 800 grit SiC paper to
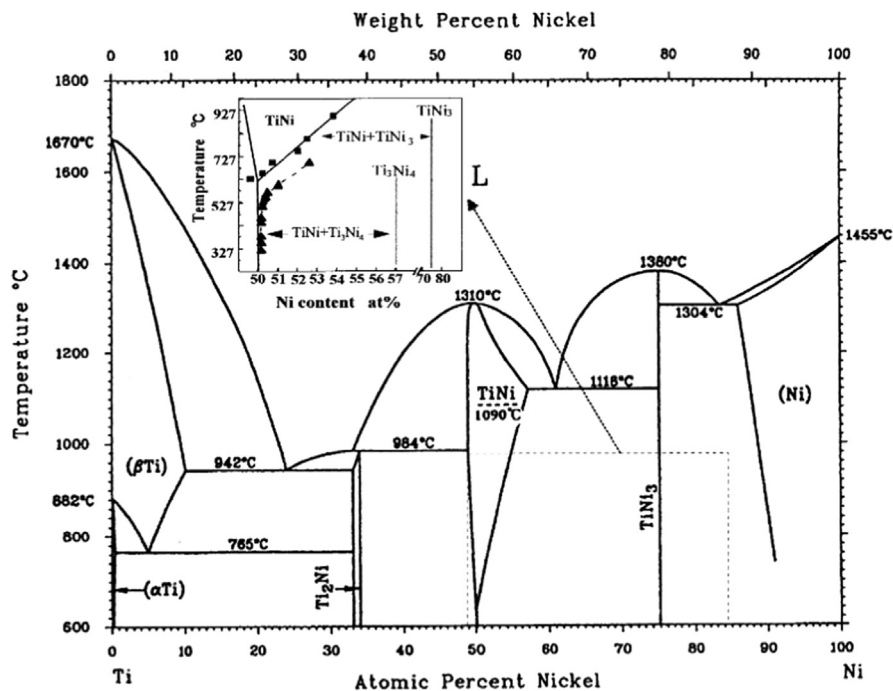

Fig. 1. Binary Ni–Ti phase diagram from [16] with the inset image showing the metastable precipitation phases [21].