

A New Method for Brazing Nitinol Based on the Quasibinary TiNi-Nb System

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[Abstract] We lay out the metallurgical basis for a new and robust method for joining NiTi shape-memory and superelastic alloys. It is based on the use of pure niobium as a melting-point depressant that can induce contact melting with NiTi at tractable temperatures. A strong, ductile, corrosion-resistant, biocompatible braze joint is achieved without the use of fluxes and allows processing in normal industrial vacuum conditions. The discovery may have far-reaching implications for the use of NiTi in complex aerospace structures, and will allow expanded use of NiTi with with dissimilar materials, including ceramics.

I. Introduction

SHAPE memory alloys (SMAs) in the NiTi family have a long history of application to aerospace problems, and have commanded a recent resurgence of interest for application to smart structures and adaptive material systems. However, the general difficulty of joining nitinol to itself has confined practical designs to relatively simple geometries with limited functionality. Various joining methods that have been investigated over the years, such as plasma, tungsten-inert gas, or resistance welding in Ar or He environments¹, and soldering², but none has achieved widespread use, at least in part due to poor reproducibility and the need for aggressive fluxes. Here we present recent results showing that NiTi can be readily brazed to itself, without fluxes, using pure niobium as a melting point depressant to cause contact liquefaction with NiTi alloys at elevated temperature.

The Ti-Ni-Nb system is already well-known as the basis for wide-hysteresis SMAs used in aerospace couplings. Niobium has very limited solubility in NiTi, and in alloys such as $Ti_{44}Ni_{47}Nb_9$ it appears³ in the form of globular bcc precipitates in a NiTi matrix. The purely mechanical behavior of these particles depresses the martensite start temperature (M_s), relative to the austenite start (A_s), and thus expands the service temperature range.

Alloys with higher Nb content have been shown to solidify into eutectic microstructures⁴. More recent data⁵⁻⁷ suggest that a quasibinary eutectic isopleth exists between the intermetallic compound TiNi and pure Nb. The eutectic isotherm is 140 K below the congruent melting temperature of NiTi, and the eutectic composition lies somewhere near $Ni_{38}Ti_{36}Nb_{26}$.

For this reason, spontaneous contact melting occurs when pure Nb comes in contact with NiTi at high temperature, and on solidification only two phases appear: austenitic NiTi and bcc-niobium. The large titanium fraction in the eutectic liquid makes it highly reactive. It readily wets NiTi surfaces, as well as many dissimilar materials including Al_2O_3 . It flows readily in to capillary spaces and aggressively dissolves surface oxides, eliminating the need for fluxes. The absence of embrittling ternary intermetallic phases in the solidified braze is conducive to good mechanical properties

We show that the solidified eutectic microstructure is in fact strong and ductile. Furthermore, with appropriate post-braze heat treatment, full shape-memory and superelastic functionality can be readily obtained in the joined NiTi sections. The technique should thus enable a wide variety of new designs that seek to exploit the special constitutive properties of nitinol in adaptive structures. In particular, new very-low-density forms of superelastic and shape-memory nitinol, such as honeycombs and space-frames, will be possible, as well as shape-

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memory/superelastic hybrid structures and novel active composite reinforcements. Perhaps as significant is the fact that dissimilar NiTi-alloy sections can be readily fused: superelastic members may be joined to NiTi castings, or NiTi foams bonded to shape-memory devices, for example.

The brazing process we have developed may be viewed as a variation on the transient liquid phase (TLP) bonding technique, which has been employed for other alloy systems⁸⁻¹⁰. In the present approach, however, heat is removed before isothermal freezing occurs, and the liquid is allowed to solidify into a eutectic microstructure. Although we have been able to make true TLP joints, sluggish diffusion in the solid state makes niobium unattractive for conventional TLP processes, unless very thin films are used.

Initial evaluation of mechanical properties of the braze metal has yielded excellent results. Single lap-shear and butt joints have displayed tensile strength approaching 0.8 GPa, and fractography has revealed microvoid coalescence and fully ductile tearing. Microstructural studies have clarified the main factors governing the evolution of microstructure (and the behavior of oxides) during the bonding process.

Before presenting further detail on the latter results, we discuss aspects of ternary phase equilibria in the Ni-Ti-Nb system, identify some rate-controlling parameters for the contact melting process, and give a preview of mechanical test results on fully superelastic NiTi sections joined with the new technique. Readers are referred to a companion paper¹¹ in this forum that gives results on open-cell honeycomb structures fabricated using the new technique. These structures are readily built up from off-the-shelf nitinol, easily processed, have relative density near 5%, and show a kinematically amplified form of shape-memory (and superelasticity) entailing strain-recovery well-exceeding 50%.

II. The Ternary Ni-Ti-Nb System

We have constructed estimates of the isothermal sections of the Ni-Ti-Nb ternary phase diagram at 20 and 900°C (Figure 1) based on current understanding of the relevant binary systems, together with data taken from references 5, 6 and 7. Five intermediate ternary intermetallic phases have been identified⁷, all residing in the Ni-rich region of the diagram. Significantly, the Ti-rich side contains no known ternary intermediate phases, a fact at least partly attributable to the complete mutual solubility of Ti and Nb at temperatures above the titanium α - β transus at 882 °C. The red line joining NiTi and Nb across the 900 degree diagram is the locus of all possible compositions of a liquid formed by contact melting between equiatomic NiTi and pure Nb (assuming solid state diffusion to be negligible). The line is also the projection of the quasibinary NiTi-Nb isopleth, discussed further below.

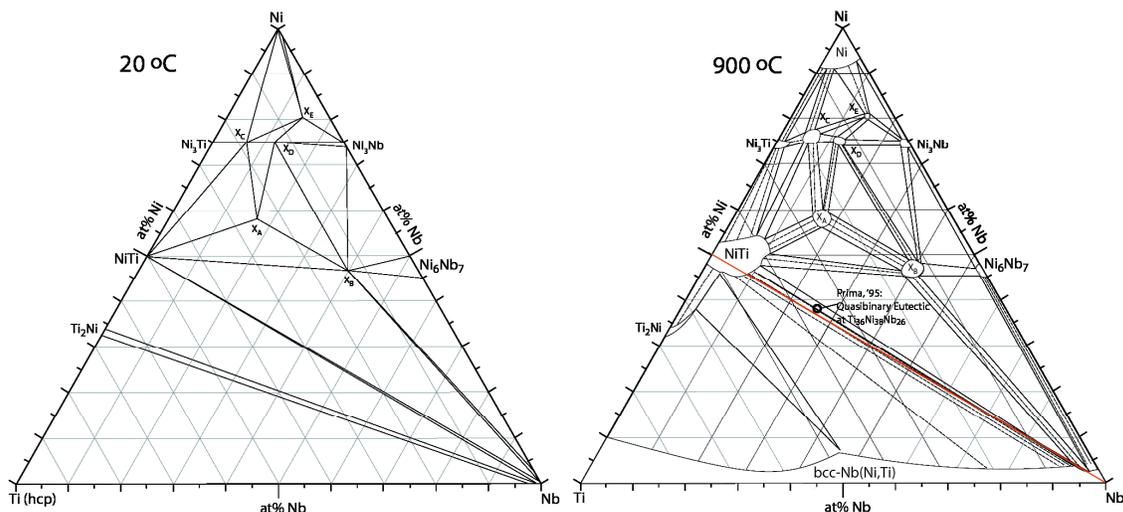


Figure 1. Estimated room temperature and 900 °C isotherms for the Ni-Ti-Nb ternary system.

Figure 2 illustrates schematically the essential features of the full Ni-Ti-Nb system near the liquidus, showing the three terminal binary systems, together with the liquidus surface, and a possible scheme for the four-phase reaction planes in which the liquid phase participates. (For this purpose it is assumed for simplicity that the ternary intermediate phases all transform congruently at temperatures below 1035 °C, consistent with - though not proven by - the available data.) Of the five reaction planes shown, the Class-II four phase equilibria¹² at U2 and U3 are of

particular significance. Both of these reaction isotherms include the liquid phase, together with both β -NiTi and bcc-niobium. The fourth phase in U2 is the compound Ni_6Nb_7 , whereas for U3, the Ti_2Ni phase completes the reaction plane. Thus, lying between U2 and U3 (in composition space) is a large region of NiTi + Nb two-phase equilibrium that is suggestive of the existence of a quasibinary eutectic system involving these terminal phases.

The quasibinary eutectic isotherm coincides with a temperature maximum associated with two lobes of the three-phase NiTi+Nb+Liq. field, arising from U2 and U3 respectively, as shown in the lower sketch in Figure 3. Here, the ternary diagram is cut along the line joining NiTi and Nb to reveal the quasibinary eutectic isopleth (rear sketch, red lines). The foreground sketch shows how the NiTi+Nb+L 3-phase field rises from U3 at 960 °C, pinches off to an isothermal maximum at 1170 °C, and then expands again as it descends before contacting U2 at 1140 °C.

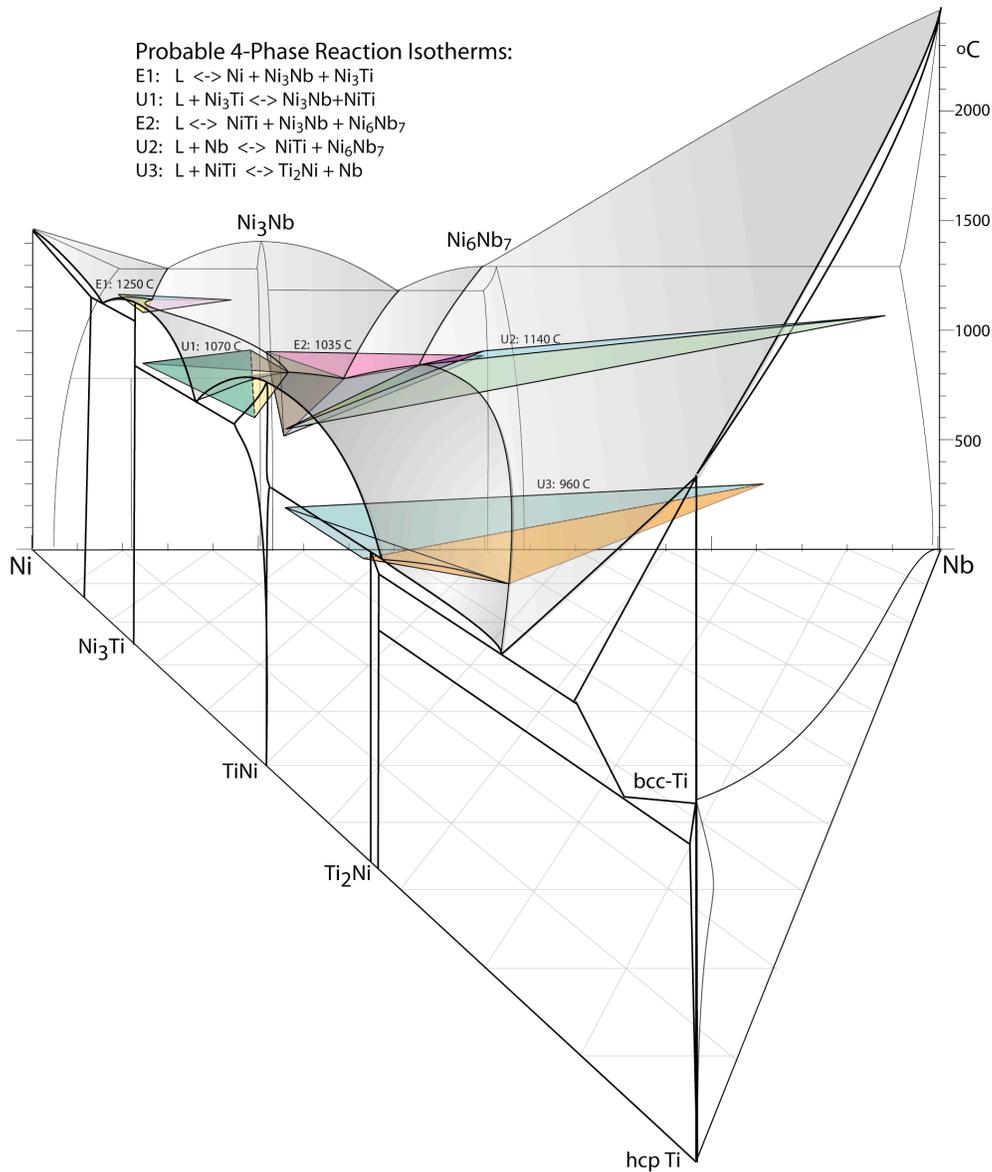


Figure 2. Schematic of the three terminal binary diagrams, the liquidus surface, and the five four-phase reaction planes involving the liquid phase in the Ni-Ti-Nb system.

Figure 4 shows our current best estimate of the features of the quasi-binary NiTi-Nb isopleth, which may in fact be a simple eutectic system as indicated in Fig. 4a (left). Although microstructural studies in the present work have not revealed phases other than B2-NiTi and bcc-niobium in the solidification products, the data^{5,7} suggest that

the quasi-binary line (the locus of equal Ni and Ti concentrations) crosses over the Ni+Ni₆Nb₇+Nb three-phase field (extending down from U2) with an intersection near 50 at% Nb at 900 °C. If this is the case, the NiTiNb system does not contain a 'perfect' quasibinary eutectic, but would rather have a slightly more complex isopleth along the lines suggested in Fig. 4b (right). This would lead to the possibility of simultaneously precipitating small amounts of both NiTi and Nb as proeutectic phases, but would otherwise lead to solidification in a very similar manner to a perfect quasi-binary eutectic system.

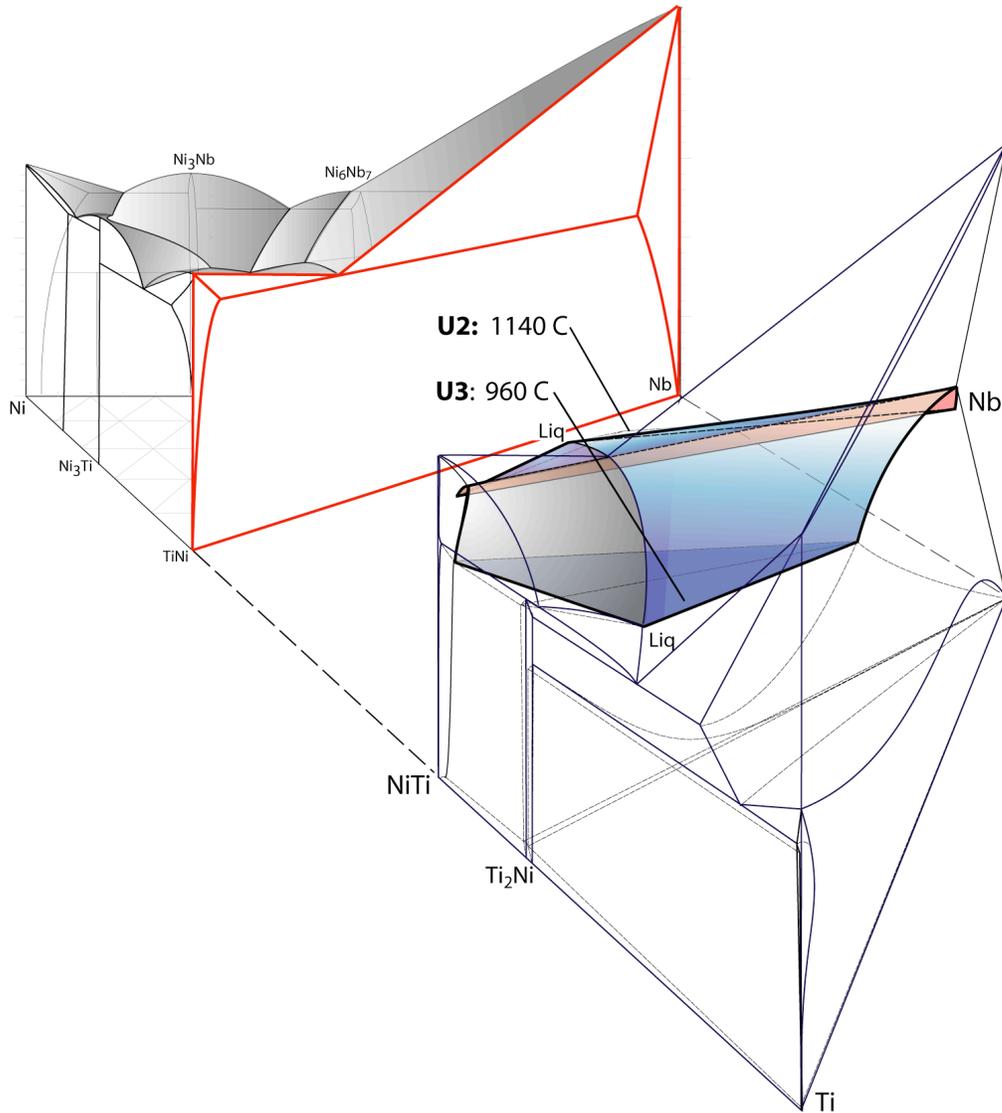


Figure 3. The Ni-Ti-Nb system cut along the line joining NiTi and Nb to reveal the NiTi-Nb quasibinary eutectic system (red lines, rear sketch), and the nature of the NiTi+Nb+L 3-phase fields on either side of the dividing line. The quasibinary eutectic isotherm coincides with degeneration of these 3-phase fields into an isothermal line at a temperature maximum of ~1170 °C.

The process of contact melting can be understood by reference to 'perfect' eutectic diagram in Fig. 4a (left). The red line here indicates a typical processing temperature for brazing (1180 °C). Ignoring the presence of surface oxides and considering the monolayers on either side of an NiTi-Nb interface (together with the relevant average surface atom densities), the local interface composition is found to be on the order of 30 at% Nb. At 1180 °C this solid-solid interface is thermodynamically unstable and contact melting occurs. If solid-state diffusion is negligible

during liquid formation (a reasonable assumption for short times when the S/L boundary is moving), the liquid composition must lie on the line in the ternary diagram joining the pure NiTi and Nb.

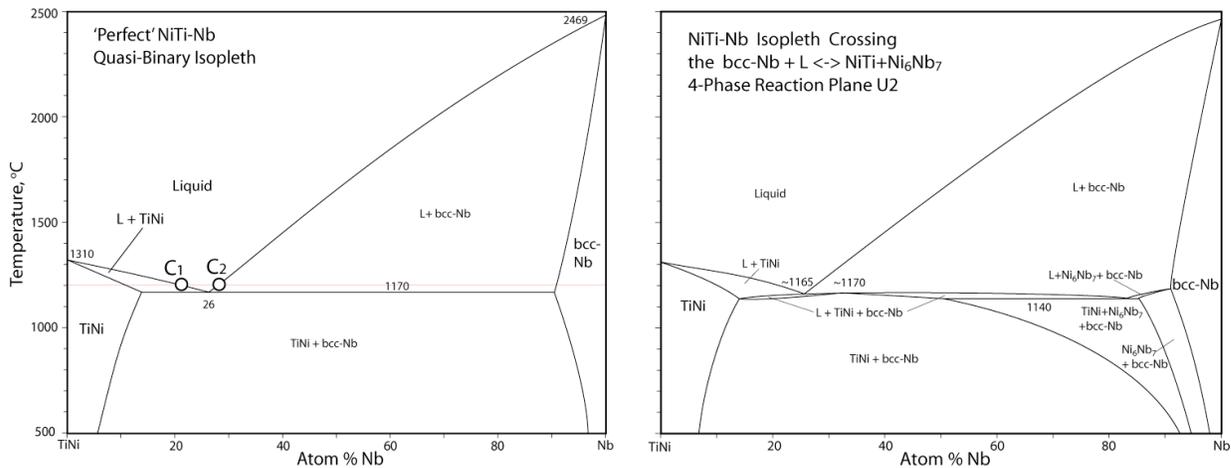


Figure 4. Possible alternative quasibinary isopleths. (a, left) Simple quasibinary case; and (b, right) the same isopleth if the quasibinary line crosses the 4-phase reaction plane U2 as indicated in Fig. 1.

Once formed, the liquid must attempt to maintain S/L interface equilibrium simultaneously with two solids (NiTi and Nb), one on each side of the liquified zone. This means that the liquid composition in contact with Nb (C2 in Fig. 4a) is richer in Nb than that at the NiTi solid-liquid interface (C1). Although the average liquid composition must lie between C1 and C2, these differing interface compositions set up a gradient in the liquid that drives cross-diffusion of NiTi and Nb between the two interfaces. As niobium, for example, diffuses through the liquid toward the NiTi interface, local equilibrium is upset there, and can only be re-established by melting an appropriate amount of NiTi, and vice-versa. In this way, melting continues (consuming about 2.2 volumes of NiTi for each volume of Nb) until the niobium is exhausted, at which point the liquid composition must rapidly move to the intersection of the process-temperature isotherm and the liquidus line on the NiTi-side (C1). Interface equilibrium can now be established and melting ceases. (Solid state diffusion of Nb into the NiTi section would subsequently lead to slow isothermal formation of a constitutional proeutectic NiTi phase, as occurs in TLP methods, but this process has been observed to be extremely sluggish at the temperatures used in these experiments.) On cooling from the process temperature, since the liquid composition (C1) is now enriched in NiTi with respect to the eutectic composition, a proeutectic NiTi phase solidifies first, followed by formation of the eutectic solid at 1170 °C.

The sequence just described is consistent with time-resolved observations (shown in Figure 5) of the development of microstructure in NiTi - Nb - NiTi couples held at 1185 °C for various times from 1 to 120 seconds and subsequently furnace cooled. At one second, melting has already progressed significantly, but the microstructure contains substantial amounts of unreacted niobium, together with eutectic NiTi+Nb and proeutectic NiTi solidification zones. As the braze time is lengthened, niobium is steadily consumed, but at a decreasing rate, until it has been exhausted after approximately 30-40 seconds at temperature. (A detail of the eutectic microstructure at the tip of one of the NiTi dendrites is shown in Figure 6.)

The rate of melting is limited by the diffusion coefficients in the liquid, and by the magnitude of the concentration gradients established by the need to simultaneously maintain equilibrium at the two dissimilar S/L interfaces. In the present case, an estimated liquid phase diffusion coefficient of $\sim 10^{-9}$ m²/s is roughly consistent with observed melting rates at 1185 °C. The diminishing rate of liquid formation over time is consistent with nominally constant diffusion coefficients, but coupled with an increasing path-length for diffusion, the latter created as more liquid forms. The net effect of increased liquid fraction is to flatten the concentration gradients.

It is also evident from Figure 5 that the relative amount of proeutectic NiTi diminishes as niobium is consumed. It is possible that this occurs because the liquid composition is itself a function of the rate of melting. Initially, when the rate is high, the liquid may be relatively enriched in NiTi, but as the rate slows, the niobium content may increase because the melting kinetics on the Nb side are inherently slower, consistent with the high melting point of Nb.

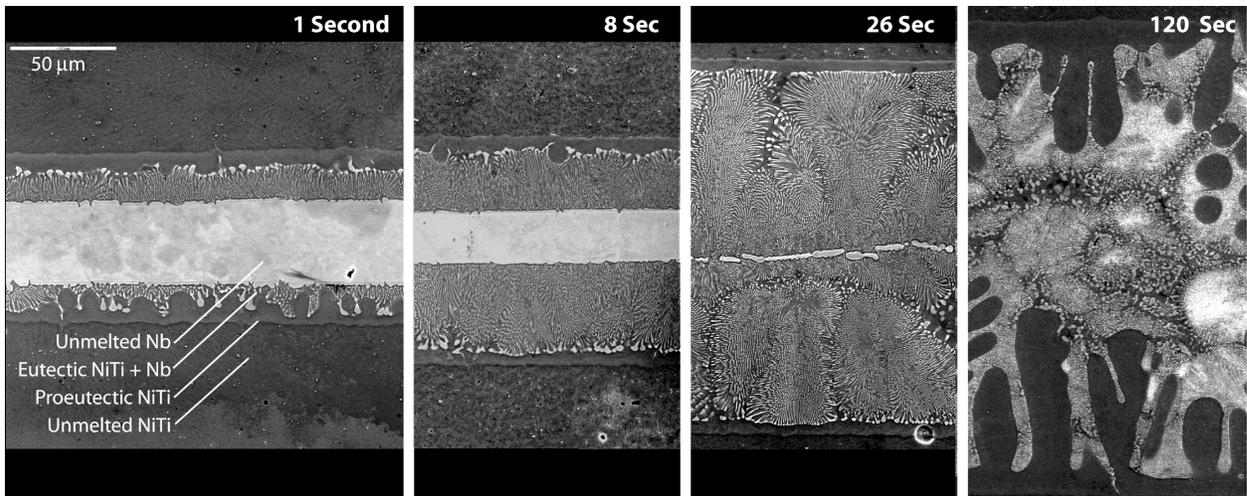


Figure 5. Time-resolved development of braze microstructure as a function of time at temperature. At 120 seconds (far right) the niobium is completely consumed.

III. Mechanical Performance

Initial tests indicate that the strength and ductility of braze joints are quite good. Figure 7 shows a typical stress strain curve for 3 mm thick superelastic nitinol plates brazed together with a butt joint at the center of the tensile specimen.

The specimen was brazed with pure niobium at 1180 °C for 6 minutes, furnace cooled, and finally annealed at 350 °C for 90 minutes prior to testing. Fracture occurred at just under 800 MPa, and the plateau associated with stress-induced martensite formation is clearly evident. The dashed line in Figure 7 shows the typical superelastic behavior observed in butt-joint specimens after a few shake-down cycles, indicating that excellent superelasticity can be obtained with proper post-braze heat treatment. The inset in the figure shows the dimpled cup-and-cone fracture surface typical of failure through the eutectic microconstituent of the braze joint, indicating that the braze material is fully ductile.

It should be pointed out that although the tensile data shown above give an accurate indication of braze ultimate strength, the yielding strains observed derive primarily from deformation of the nitinol portion of the gage length used, and the yield strength and ductility of the braze are not probed directly by this test. That the braze is highly ductile is, however, strongly suggested by the fully dimpled fracture surfaces. It is likely, however, that the yield strength of the braze filler is not as high as might be desired, and work is ongoing to investigate solution and precipitation-hardening schemes for the braze metal. It is likely that the latter is controlled by the soft niobium phase in the eutectic.

As mentioned earlier, the eutectic liquid readily dissolves many oxides, which therefore become incorporated into the melt and may precipitate as detrimental oxide inclusions. We have frequently observed Ti_2Ni precipitation under particularly heavy oxidation conditions (thick prior oxides or poor furnace vacuum). It is of interest therefore to develop microalloying strategies to suppress the formation of this phase. Some success along these lines has recently been achieved via additions of ~1%

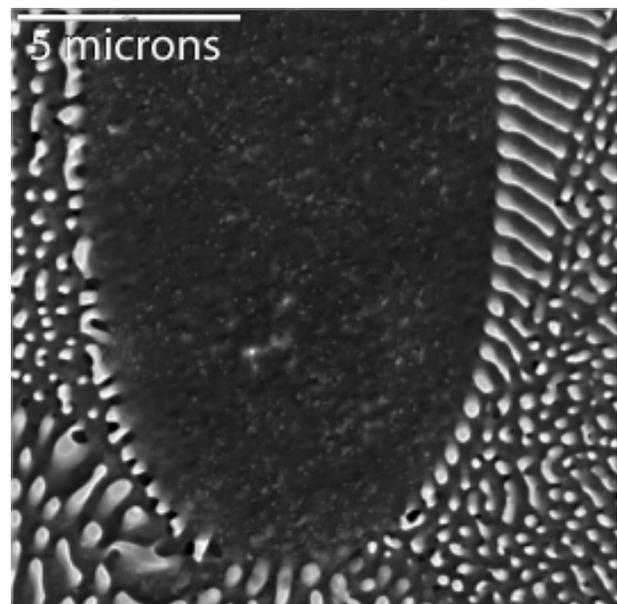


Figure 6. Braze microstructure showing the tip of a proeutectic dendrite and the surrounding eutectic microconstituent. Note that the eutectic structure forms in both rod and plate morphologies. The rods are believed to derive from solid-state ‘spheroidization’ of the plates.

Zr to the niobium braze foil. This may be done by PVD methods, but can also be accomplished by use of Nb-1Zr foils which are commercially available.

Conclusion

It is shown that pure niobium functions as a melting point depressant for NiTi and that the quasibinary eutectic nature of NiTi-Nb equilibrium forms the basis of a robust brazing technique for joining NiTi sections. Excellent strength, toughness, and transformational functionality can be obtained in a low-cost batch process that will allow for a variety of new topologies to be realized from conventional wrought NiTi precursors.

Acknowledgments

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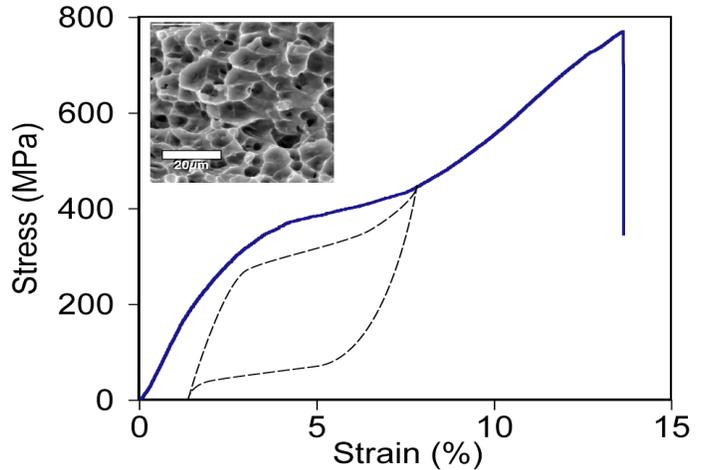


Figure 7. Stress-strain curve for butt-joined 3 mm superelastic NiTi plates showing near-800 MPa strength in the braze. The dashed line shows typical superelastic cycling observed in such specimens after a few shakedown cycles that have introduced a small amount of permanent strain. The inset is an electron micrograph showing the fully ductile fracture surface indicative of ductile tearing by microvoid coalescence.

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