Multicomponent Nitinol for Orthodontic Applications

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Fort Wayne Metals desires to understand the effects of Copper addition to Nickel-Titanium (Nitinol) shape-memory alloy for dental wire. A heat treatment plan was developed to homogenize the as-cast alloy for compositional uniformity, and subsequent mechanical testing compared ternary Ni-Ti-Cu wire produced to the treatment plan with standard binary Nitinol wire. Compositional analysis of the homogenized material showed microsegregation was less than the as-cast material, but no conclusive trends were seen in microsegregation reduction for different heat treat temperatures and times. Tensile testing does show that Copper addition benefits the mechanical properties of Nitinol through a reduction of the stress hysteresis and increases in elastic modulus, ultimate tensile strength, and yield stress.

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Project Background

The binary 55Ni-45Ti wt.% alloy Nitinol is an alloy with shape memory effects, which involves deformation of a material followed by a temperature-activated restoration of the original shape. For the Nickel-Titanium system, the system begins in a twinned martensitic structure and phase-transforms to standard martensite upon stress from deformation. Once external heat is applied to the system, the martensite phase-transforms to austenite to relieve the stress, then cools to reform the twinned martensite and regain the original shape[1].

The addition of Copper to the Nickel-Titanium system promises to improve the final product through a smaller hysteresis response in the cyclic phase transformations[2], consistency in the plateau of hysteresis, and a narrower region of response[3]. This occurs as Copper substitutes into the Nickel-Titanium lattice structure, promoting orthorhombic B19 martensite over monoclinic B19` martensite[2]. This precise, consistent control of the material response is highly desirable for the orthodontic applications Nitinol is used in, as low-magnitude forces applied consistently over time avoid tissue damage during tooth movement[3].

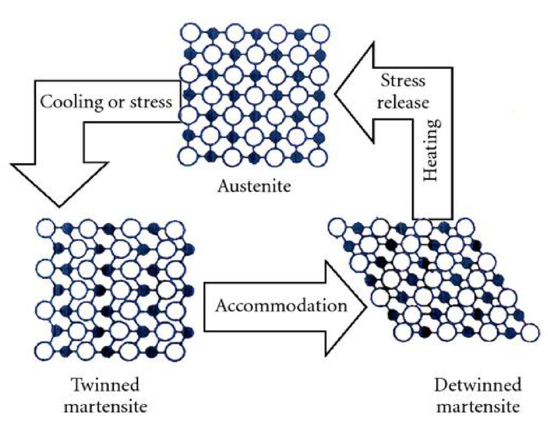

Figure 1: Cyclic phase transformations characteristic of the shape memory process. Retrieved from Fernandes et al.

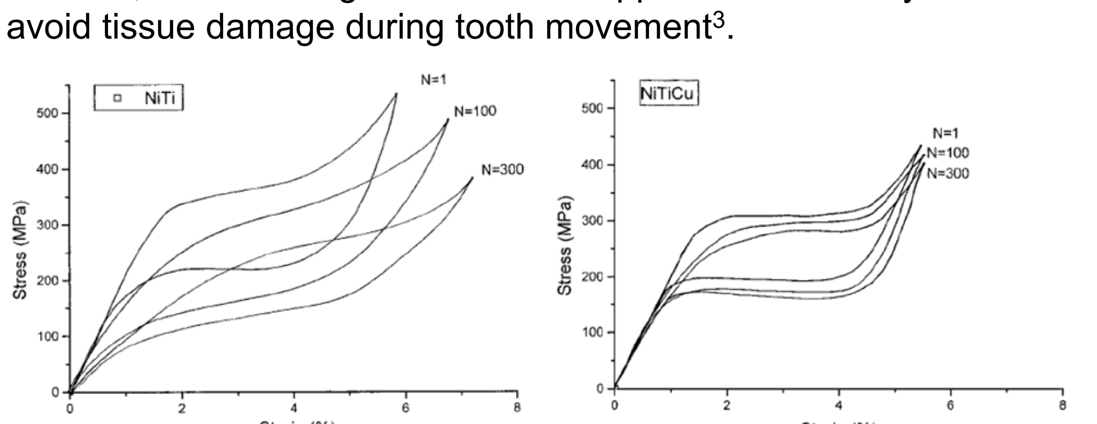

Figure 2: Stress-strain hysteresis loops for binary Nitinol (left) and Copper-doped Nitinol (right) over a cyclic loading regime, demonstrating the consistency of response and reduction in activation stress. Retrieved from Gil and Planell.

Experimental Procedures

The homogenization heat treatment experiments were performed using cast discs of 49Ni-45Ti-6Cu wt% sectioned into quarters with a radius of approximately one inch, supplied by the Fort Wayne Metals team. Homogenization proceeded using a high-temperature furnace, with a temperature ramp rate of 10°C per minute. Hold times and temperatures are detailed at left in Table 1.

Table 1: Test matrix of homogenization times and temperatures tested. Number values 1-6 indicate the order of testing, starting with Sample 1.

Temp (°C)	Time (hours) 48	Time (hours) 72
900	6	2
950	-	3
1000	-	4
1050	5	1

Upon completion of heat treatment, alloy samples were sectioned, mounted in Bakelite, and metallographically polished to a mirror finish for Scanning Electron Microscopy (SEM) analysis. SEM was performed with a NanoScience Phenom desktop machine, capable of Energy Dispersive Spectroscopy (EDS). SEM images were taken using back scatter detection mode at 2,200x magnification. A 22x22 square grid of points spaced 4.15µm were analyzed using EDS. This spacing was selected as it resulted in a grid that was larger than any of the largest features in the microstructure and the spacing is on a similar scale to the smallest features. Primary data analysis was performed with a standard deviation calculation for the compositions of Ni, Ti, and Cu for each sample.

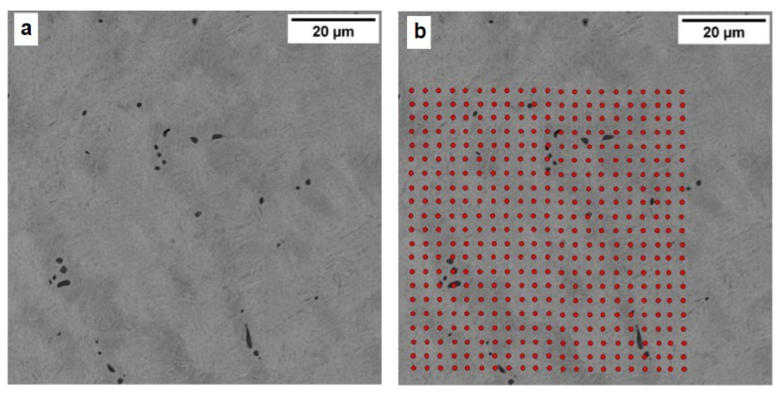

Figure 3: Backscatter SEM images taken of an As-Cast ternary Nitinol sample, showing a) the original surface features and b) a visualization of the scan grid overlay, demonstrating the approach taken to EDS analysis.

Subsequent tensile tests were conducted on an MTestQuattro load frame set up to pull wire in tension at a 5 mm/minute displacement rate. Load + unload + pull-to-failure tensile tests were performed on heat-treated binary Nitinol and the ternary NiTiCu samples produced according to the recommended parameters. These tests were performed on by pulling the wire until a specified load, unloading at the same rate until stress was close to 0, and then loading again until failure. Six samples were tested per material to adequately characterize each material's stress-strain and hysteresis behaviors.

Homogenization Results

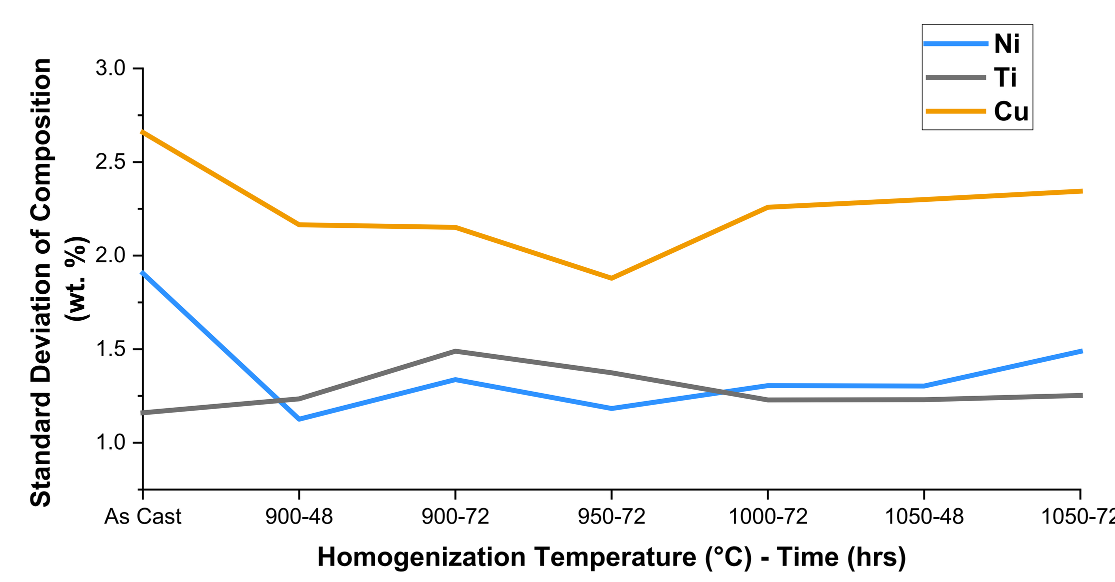

Figure 4: Standard Deviations reported for each element at each homogenization parameter combination tested. Nickel Standard Deviation is shown in blue, Titanium in gray, and Copper in orange. Left to right on the plot proceeds from untreated, as cast material to maximum time and temperature, with time incrementing from lowest to highest within a temperature range in the series before temperature increases.

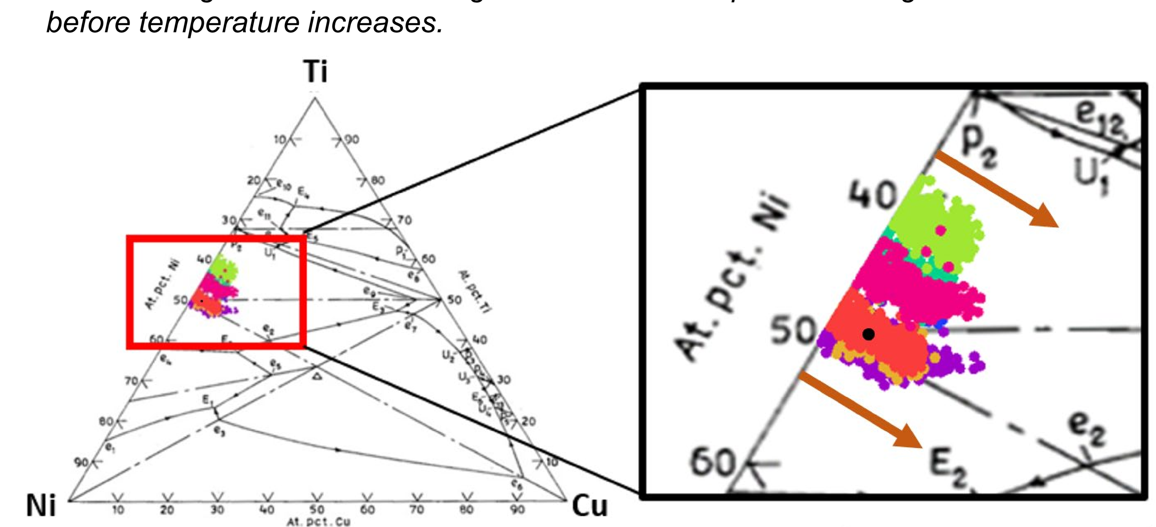

Figure 5: Plot of every individual data point from the EDS point scans on a ternary phase diagram liquidus projection map of Ni-Ti-Cu. The image on the right is a magnification of the outlined region in the image on the left. The brown arrows indicate general direction of the solidification path as the samples were cast, such that the arrow heads are pointing in the direction of last solid to solidify and the black dot represents the nominal composition of the alloy.

Tensile Testing Results

Provided ternary wire was homogenized at 1050°C for 48 hours.

Table 2: Averages of reported mechanical properties from tensile testing of the binary Nickel-Titanium and ternary Nickel-Titanium-Copper Nitinol alloys.

Alloy	Modulus of Elasticity (GPa)	Ultimate Tensile Stress (MPa)	Yield Stress (0.3% offset) (MPa)	Stress Hysteresis (MPa)
Binary NiTi	45	1484	411	411
Ternary NiTiCu	51	1548	432	86

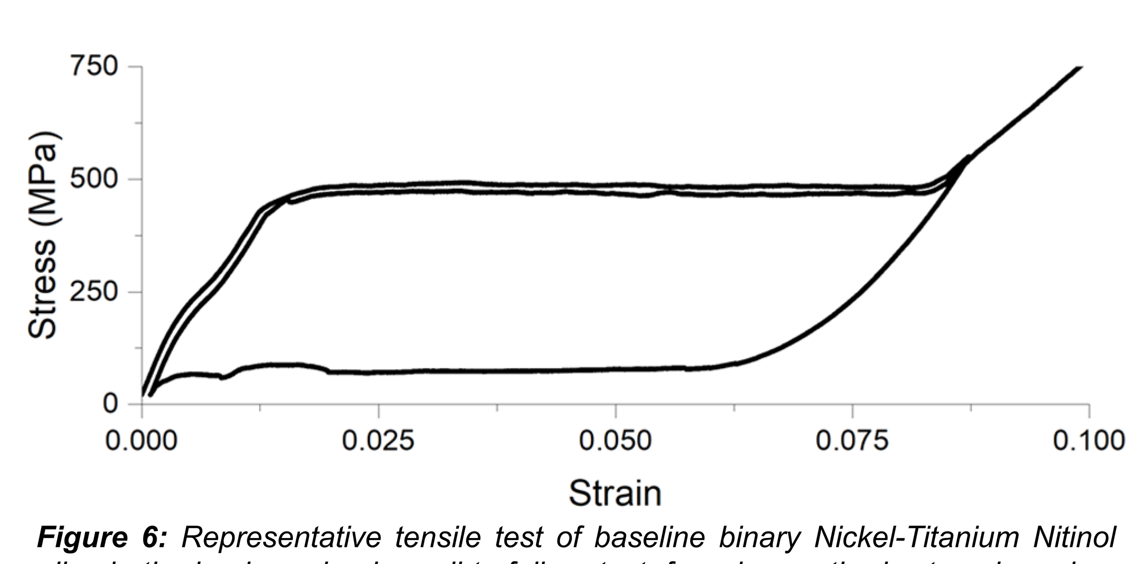

Figure 6: Representative tensile test of baseline binary Nickel-Titanium Nitinol alloy in the load + unload + pull-to-failure test, focusing on the hysteresis region. Binary Nitinol is shown to exhibit a broad hysteresis span prior to pulling to failure. Failure behavior is not shown, as the results of failure can be understood from the data in Table 2.

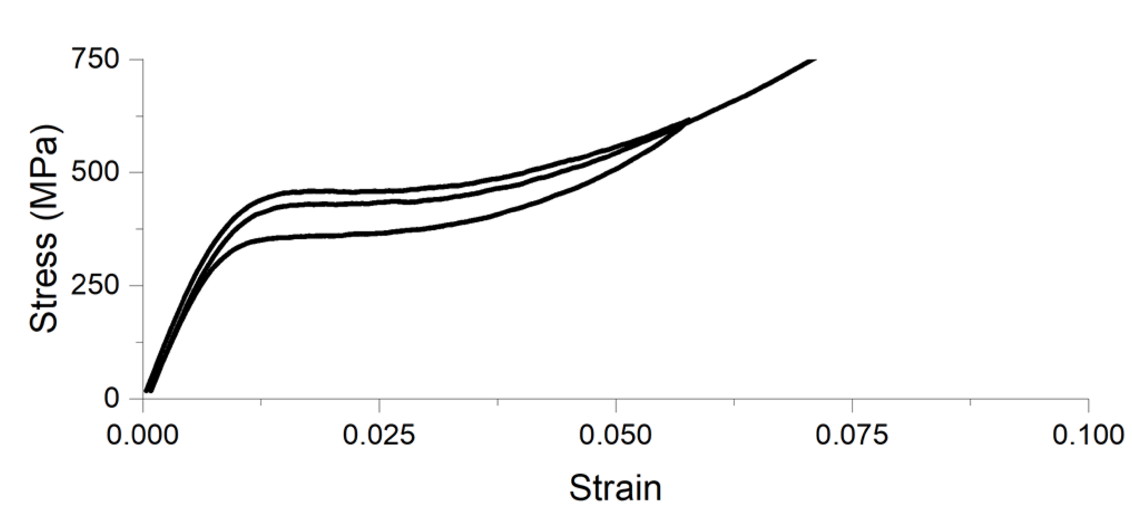

Figure 7: Representative tensile test of experimental ternary Nickel-Titanium-Copper Nitinol alloy in the load + unload + pull-to-failure test, focusing on the hysteresis region. Ternary Nitinol is shown to exhibit a narrow hysteresis span prior to pulling to failure. Failure behavior is not shown, as the results of failure can be understood from the data in Table 2.

Homogenization Discussion

The standard deviation data was expected to show the as-cast sample as having the largest standard deviation of composition for all elements, after which the standard deviations would decrease as time and temperature of homogenization increased. Figure 3 shows that the as-cast sample did have a higher standard deviation of Ni and Cu content, but not Ti, and there was no clear downward trend as time and temperature of homogenization increased. Also, the standard deviation for all samples is small relative to the potential composition ranges that would develop if the data represented the entire solidification path all the way to appropriate eutectic.

Figure 4 shows that Cu tends to substitute for Ni and Ti equally throughout the solidification process in the samples. Since all samples have the sample nominal composition, differences in average composition of the data points would likely indicate microsegregation. The shape of all data points appears to drift towards the Ti rich portion of the diagram, suggesting Ti is the element responsible for microsegregation. It is possible that during solidification, Ti rises to the top of the melt and travels away from the solidification surface, due to its lower density. Since Ti should partition into the solid, this flow of Ti away from the solidification surface could lead to Ti content being underrepresented near the bottom of the buttons and overrepresented in the top of the buttons. Thus, the selected region of analysis could yield results varying in Ti content due to representing different depths within the button. This could be a confounding variable when analyzing the trends (or lack thereof) in the standard deviation data.

Tensile Testing Discussion

Copper addition overall improved the mechanical properties of nitinol. The elasticity of the ternary alloy is 12% higher than the binary nitinol, the UTS is 4% higher, and the yield strength is 5% higher. Most importantly, the stress hysteresis is 80% lower than the binary. Overall, all these changes are favorable for dental wire applications.

Conclusions

Using data that seemed conclusive at the time, our group initially recommended homogenization at 1050°C for 48 hours. However, the EDS software used to analyze the data was found to be out of date, invalidating the previous data. Newly collected results after the software update showed evidence of a general reduction in microsegregation after heat treatment, but little to no difference between different heat treatment temperatures and times tested. This result suggested that the time could be 48 hours, and perhaps the temperature could be lowered from 1050°C.

The mechanical testing showed Copper does improve the mechanical properties. Ternary Nitinol exhibits a narrower hysteresis region than the binary, providing the more consistent stress response desirable for orthodontic applications. The UTS and yield strength are also higher in the ternary alloy.

Recommendation to Sponsor

Overall, our group found that ternary nitinol homogenized at 1050°C for 48 hours performed better mechanically than non-homogenized binary nitinol. Further mechanical testing comparing homogenized and non-homogenized ternary nitinol is recommended to determine the effects of chemistry and heat treatment on the mechanical property improvements. Our group also recommends testing shorter heat treatment times and lower temperatures to see if the improvements can be maintained more economically.

References

1. Fernandes, D.J. et al. (2011) *Understanding the shape-memory alloys used in orthodontics*. ISRN dentistry vol. 2011: 132408.
2. Otsuka, K., Ren, X. (1999) Recent developments in the research of shape memory alloys. Intermetallics, Volume 7.
3. Gil, F.J., Planell, J.A. (March 1999) Effect of copper addition on the superelastic behavior of Ni-Ti shape memory alloys for orthodontic applications. Journal of Biomedical Materials Research.