Consideration of the ASTM Standards for Ni - Ti Alloys*

Frank Sczerzenie

Special Metals Corporation

* to be published in SMST-2004: Proceeding of the Second European Conference on Shape Memory and Superelastic Technologies, edited by Meertman and Fischer, Baden Baden, October, 2004.

ABSTRACT

ASTM Standards F2004, F2005, F 2063 and F2082 have been issued for binary Ni – Ti alloy raw materials for use in medical devices. Thermal analysis and chemistry data are presented on nine binary alloys ranging in nickel content from 54.8 to 56.1 weight percent nickel. Analysis of differential scanning calorimetry data shows that the standard deviation of transformation temperature parameters, M_f, M_p, M_s, A_s, A_p and A_f are affected by the alloy formulation. The standard deviations of the parameters increase as the alloy nickel content increases. Recommendations are made for the future modification of the alloy specifications.

KEYWORDS: Nitinol, Transformation Temperature, Differential Scanning Calorimetry, Melting, VIM/VAR

INTRODUCTION

ASTM Standards F2004, F2005, F 2063and F2082 have been issued to control the manufacture and testing of binary Ni – Ti alloy raw materials for use in medical devices. Some work has been done toward determining the precision to which transformation temperatures can be measured. In the context of these efforts, it became apparent that the tolerance to which the raw material can be controlled may vary for the several binary alloys being considered. This paper is an attempt to quantify this variability.

The relationship between chemistry and transformation temperature for Ni – Ti alloys has been known for many years. Melton exhibited the effects of both chemistry and heat treatment on transformation temperatures in 1990.[1] Transformation temperature is very sensitive to the Ni:Ti ratio (see Figure 1).

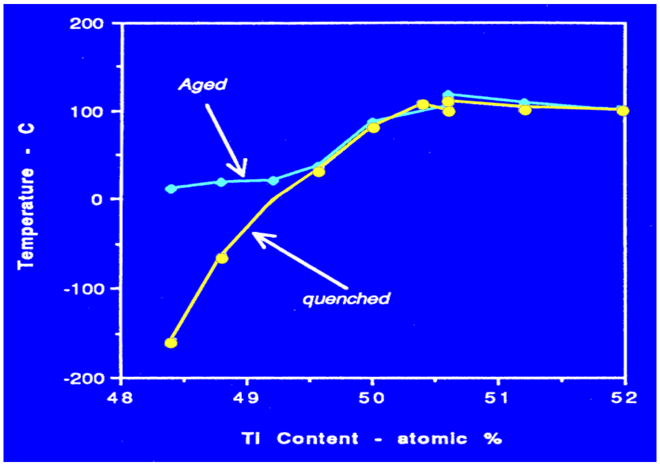

Figure 1: A_s temperature of Ni – Ti Alloys.

It has been recognized for many years that Ni – Ti alloy formulation cannot be adequately controlled by chemical analysis.[3] Therefore transformation properties are measured directly. Chemistry is very important for alloy performance, but chemical analysis is not used to control the product.

The relationship between chemistry and transformation temperature is complicated by the precipitation of second phase in nickel rich alloys. Aging at temperatures below 820°C precipitates Ni rich phases that deplete the matrix of nickel thereby raising the transformation temperature of the alloy. Aging kinetics have been discussed by Nishida[2]. For this reason there is a concern for the cooling rate of the material from a solution anneal.

Setting aside the aging effects, the Figure 1 curve for fully solutioned alloys has significant implications for commercial alloy production. In a perfectly homogeneous product, transformation temperatures would be perfectly uniform. Typical commercial products exhibit a range of transformation temperatures. Assuming that a precise, reproducible test for transformation temperature is being used, the variations in transformation temperature imply that chemistry variations exist in wrought products.

Consideration of the change in slope of the transformation temperature versus chemistry curve in Figure 1 leads to the hypothesis that, for constant variation in chemistry within ingots that differ by alloy formulation in terms of Ni to Ti ratio, the variation in transformation temperature will increase as the ingots are made more nickel rich to achieve lower transformation temperatures. The purpose of this paper is to assess the variability of transformation temperature in commercial materials.

Since 1997, thermal analysis of Ni – Ti alloys by differential scanning calorimetry (DSC) has been under scrutiny by the ASTM Sub Committee for Materials for Medical Devices[4]. Standard test method F2004 was issued for use in 2000[5]. Work is ongoing to determine the precision and bias of this test method.
In support of this effort, a series of tests was performed to assess the reproducibility of transformation temperature in one spool of wire tested in a single laboratory. This data serves as background for evaluating the data from different production alloys.

PROCEDURES

Multiple samples from a single spool of wire were tested in the lab at Special Metals. At that time, the standard anneal for 2.16 mm diameter wire was to heat treat a 40 milligram sample at 850°C for 3 minutes followed by an air cool in a dry stainless steel beaker. Since the quench rate from the heat treatment was a concern for the ASTM Task Group, duplicate tests were done on samples that were water quenched.

All of the data for the analysis of the effect of the alloy formulation was taken from production ingots made from 1995 through 2003 by vacuum induction melting (VIM) followed by vacuum arc remelting (VAR). The process is described as “bundled VAR” since the VAR electrode is constructed from several smaller ingots made by VIM. Bundling optimizes the utilization of VIM material by mixing the transformation temperature highs and lows in the molten ingot pool and thereby reducing the range of the transformation temperatures in the VAR product compared to that measured in the VIM pieces.

DSC is done on every VIM heat and at critical steps during subsequent processing. In 1995, individual VIM heats were 14 Kg, electrodes for VAR weighed 800 Kg and VAR ingots were 300 mm in diameter. In 2003, individual VIM heats weigh in excess of 180 Kg, VAR electrodes weigh in excess of 1600 Kg and VAR ingots are 355 mm in diameter. After VAR, the ingots are hot forged to a rectangular billet, conditioned, reheated and hot rolled to bar or coil. Wire is cold drawn from coil.

The alloy aging effects shown in Figure 1 and described above necessitate careful and consistent sample preparation for thermal analysis. DSC was performed by a fixed procedure that pre-dates the ASTM standard. The procedure is consistent with the ASTM standard in every respect except the heat treatment time for wire samples. Beginning in 1989, the procedure used for wires had a shorter heat treat time. For the sake of consistency, this time was not changed for these tests.

Binary alloys were characterized by the A_s in the fully annealed condition. Nine alloys were evaluated with A_s temperatures of +95 °C, +55 °C, +30 °C, +5 °C, 0 °C, -10 °C, -15 °C, -25 °C and -50 °C. Each data set was reviewed for outlier data points. For example, large variations in transformation temperature can occur at the very top or bottom of the VAR ingot. This has been correlated to variations in macrostructure. Therefore outlier data from the bottom of the bottom billet or coil was removed from the data sets.

The average and standard deviation of each transformation temperature parameter was calculated and graphical techniques were used to determine if the data distributions were normal or skewed. For normal distributions, we expect +/- 3 standard deviations to be the 99% confidence range for each alloy.

RESULTS

Table 1 shows the results of eighteen tests on one spool of wire weighing 4.5 Kg. The standard deviation for A_s is 0.2 degrees for both data a sets and all of the standard deviations are less than one degree. The standard deviations increase as the parameter diverges from A_s.

Table 1. Pre-Test of C7-7105-2A Redraw Wire with Solution Heat Treatment of 850°C, 3 Minutes

	Weight	Cooling*	Mf	Mp	Ms	As	Ap	Af
Sample	(mg)		°C	°C	°C	°C	°C	°C
Lead 1	41.3	AC	-37.4	-27.3	-23.5	-11.4	-2.6	-0.1
Lead 2	41.4	AC	-38.5	-28.6	-23.7	-11.7	-1.9	1.1
Lead 3	40.2	AC	-36.9	-27.6	-23.2	-11.5	-2.2	0.9
Middle 1	38.1	AC	-38.2	-28.0	-23.9	-11.8	-2.5	0.4
Middle 2	42.9	AC	-37.9	-28.0	-24.1	-12.1	-2.7	0.5
Middle 3	38.6	AC	-37.1	-27.3	-24.0	-11.9	-3.1	0.1
Tail 1	35.4	AC	-37.2	-27.1	-23.6	-11.7	-3.1	-0.5
Tail 2	35.2	AC	-36.8	-27.1	-24.0	-11.5	-2.9	0.1
Tail 3	36.2	AC	-36.9	-27.8	-23.8	-11.8	-2.6	0.9
Average	38.8		-37.4	-27.6	-23.8	-11.7	-2.6	0.4
STDEV	2.8		0.6	0.5	0.3	0.2	0.4	0.5
	Weight	Cooling*	Mf	Mp	Ms	As	Ap	Af
Sample	(mg)		°C	°C	°C	°C	°C	°C
Lead 1	42.4	WQ	-35.0	-25.4	-18.2	-6.3	3.5	7.4
Lead 2	35.9	WQ	-33.9	-24.3	-17.8	-6.4	3.1	6.5
Lead 3	39.4	WQ	-34.4	-24.7	-17.8	-6.1	3.5	7.0
Middle 1	39.5	WQ	-34.5	-24.7	-18.0	-6.7	2.7	6.4
Middle 2	41.6	WQ	-35.2	-25.3	-18.5	-6.6	2.9	6.5
Middle 3	36.2	WQ	-34.8	-25.1	-18.3	-6.2	3.3	6.7
Tail 1	37.3	WQ	-33.5	-24.2	-17.5	-6.4	3.0	6.4
Tail 2	41.5	WQ	-34.4	-24.6	-17.9	-6.5	3.0	6.6
Tail 3	39.5	WQ	-33.9	-24.3	-17.8	-6.3	3.1	6.5
Average	39.3		-34.4	-24.7	-18.0	-6.4	3.1	6.7
STDEV	2.4		0.6	0.4	0.3	0.2	0.3	0.3

*Cooling: AC = air cool, WQ = water quench.

Table 2 shows the statistical analysis of the nine alloy data sets with chemistries. The magnitude of the standard deviation varies by alloy and by transformation temperature parameter. In 8 of the 9 the data sets, the A_s has the smallest standard deviation.

Table 2. Standard Deviations of Transfomation Temperature for Ni - Ti Alloys.

Aim A_s (^{o}C)	Product Form	# of Heats	# of Tests	Ni wt %	C wt%	O wt%		M_f ^{o}C	M_p ^{o}C	M_s ^{o}C	A_s ^{o}C	A_p ^{o}C	A_f ^{o}C
+95	All	19	272	54.79	0.032	0.020	Average	61.4	70.0	82.7	93.8	107.2	113.3
				0.12	0.003	0.003	STDEV	2.4	2.2	1.6	1.7	1.9	2.7
+55	All	4	85	55.32	0.034	0.021	Average	24.6	33.5	40.2	53.7	69.7	74.4
				0.06	0.002	0.002	STDEV	5.4	4.2	2.0	1.7	3.0	3.7
+30	Redraw	2	99	55.58	0.037	0.020	Average	1.0	9.7	16.6	29.5	42.7	49.8
				0.01	0.002	0.002	STDEV	8.4	6.5	3.4	2.1	4.0	3.9
+5	All	15	951	55.80	0.033	0.023	Average	-24.9	-14.9	-8.5	5.7	16.8	24.0
				0.08	0.005	0.005	STDEV	9.0	6.7	4.3	2.8	4.0	4.7
0	All	12	921	55.82	0.033	0.022	Average	-29.0	-18.9	-12.8	1.0	11.8	18.0
				0.02	0.003	0.003	STDEV	7.7	5.6	3.4	2.4	3.8	4.8
-10	All	48	1436	55.90	0.031	0.020	Average	-38.5	-27.9	-22.8	-9.4	0.4	5.8
				0.05	0.004	0.004	STDEV	9.0	6.5	4.3	2.8	3.2	5.2
-15	Bar	23	171	55.91	0.032	0.023	Average	-40.7	-29.1	-25.5	-16.0	-6.6	-0.5
				0.05	0.004	0.006	STDEV	3.9	3.2	3.9	2.6	2.5	4.4
-25	All	63	2429	55.98	0.030	0.021	Average	-53.7	-41.5	-36.1	-23.4	-13.4	-8.3
				0.03	0.004	0.006	STDEV	6.8	5.5	4.7	4.1	4.3	5.3
-50	Bar, Coil	17	121	56.10	0.030	0.022	Average	-82.4	-67.6	-61.0	-51.8	-39.8	-31.1
				0.05	0.004	0.004	STDEV	8.1	6.3	8.0	6.0	4.7	5.4

Table 3 shows a breakdown of transformation temperature data by product form for the alloy at A_s = -25 ^{o}C. In this case VIM electrode data was included in the analysis for comparison to the VAR product.

Table 3. Standard Deviation of Transfomation Temperature for Various Product Forms at A_s = -25^{o}C

Product Form	Sample Form	Number of Heats	Number of Tests		M_f ^{o}C	M_p ^{o}C	M_s ^{o}C	A_s ^{o}C	A_p ^{o}C	A_f ^{o}C
VIM	Roll-Down	172	172	Average	-51.5	-37.4	-33.6	-26.5	-15.5	-7.4
				STDEV	8.1	7.6	9.1	7.0	6.3	8.2
VAR(Bar)	Roll-Down	62	468	Average	-55.9	-42.1	-35.2	-25.0	-13.5	-6.1
				STDEV	7.5	6.5	5.4	3.9	3.9	5.0
Coil	Coil	22	174	Average	-47.6	-36.7	-33.0	-20.8	-13.0	-9.1
				STDEV	4.9	4.1	4.0	3.3	3.3	3.6
Redraw	Wire	27	1657	Average	-53.7	-41.7	-36.6	-23.3	-13.4	-8.9
				STDEV	6.4	5.0	4.1	3.8	4.0	4.7
All Wrought	See Above	69	2746	Average	-53.7	-41.5	-36.1	-23.4	-13.4	-8.3
				STDEV	6.8	5.5	4.7	4.1	4.3	5.3

Graphical analyses were done on the data distributions for alloys at A_s = +95°C and A_s = -25°C. This is shown in Figures 2 and Figure 3 respectively. Figure 4 shows the effects of the alloy formulation on the standard deviations of the transformation temperature parameters for all of the alloys.

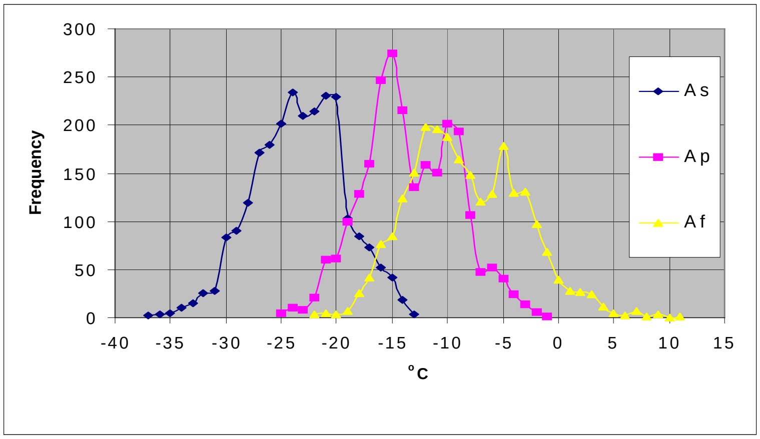

Figure 2. Distribution of transformation temperature parameters for A_s = -25°C alloy.

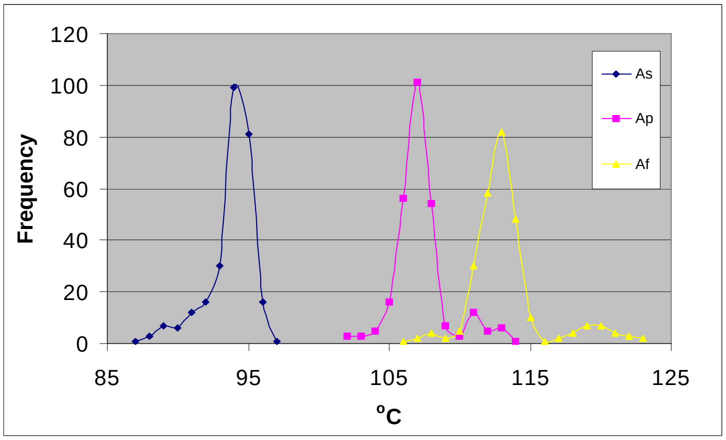

Figure 3. Distribution of transformation temperature parameters for A_s = +95°C alloy.

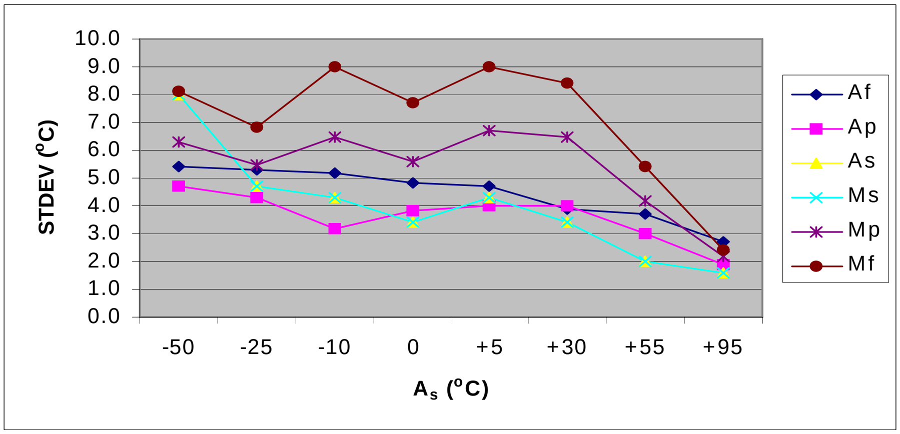

Figure 4. The variation of the standard deviation of A_s.

DISCUSSION

The thermal analysis data in Table 1 shows a very reproducible test under controlled conditions. The results are very sensitive to the cooling rate of the sample from the anneal for a 40 milligram sample. The water quenched samples have a higher transformation temperature. This is contrary to the hypothesis that slow cooling would allow greater precipitation and raise the transformation temperature of the alloy matrix. Therefore, it is hypothesized that water quenching quenches in defects that impede the transformation reactions.

Segregation in the 4.5 Kg spool of wire is small and by inference short range segregation has a small effect on the range of transformation temperatures found in large ingots. Both sets of data in Table 1 show that the standard deviation of the transformation parameter increases from As to Ap to Af and from As to Ms to Mp to Mf. This suggests some systematic effect of the test technique on these parameters. This was also seen in the alloy data as discussed below.

All of the standard deviations in the Table 2 alloy comparison are one order of magnitude larger than those obtained in the evaluation of thermal analysis technique. Therefore the variations obtained in the alloy data may be attributed to variations in sensitivity to alloy formulation.

In Table 3, the standard deviations of the transformation temperature parameters vary by parameter and by product form. A comparison of the standard deviations from VIM and from VAR at A_s = -25°C confirms that bundling reduces the variability of the product. Table 3 also shows an increase in the average A_s at coil. Similar increases in A_s at coil were observed in other high Ni products. This may be the combined effect of residual aging in the sample from the hot rolled coil and a change in the sample form. VIM electrode and hot forged bar are tested by making a hot rolled sheet sample from the product. Samples for coil are cut directly from the hot rolled coil. Samples for wire are cut directly from the cold drawn wire. Therefore a longer annealing time may be needed for hot rolled coil.

The data distributions illustrated graphically at A_s = -25oc in Figure 2 and at A_s = +95°C in Figure 3 have some similarities and some differences. For both alloys, the A_s curves approaches a normal distribution but has a tail toward lower temperatures. For both alloys the A_p and A_f curves tail toward higher temperatures. This may be due to the nature of the DSC test and the effects of the thermal impedance between the sample and the thermal analysis test equipment.

The curves at A_s = +95^{o}C are very sharp and narrow whereas the curves at A_s = –25^{o}C are broad and erratic. This is in part due to the differences in the size of the data sets. However, the variability of the VIM material in relationship to the greater sensitivity of transformation temperature to chemistry and aging at higher nickel contents is the dominant factor causing this difference.

Figure 4 shows the trends in standard deviations with respect to the alloy. The standard deviations of the Mp and Mf vary more erratically than for the other parameters. The standard deviation of A_s varies from a minimum of 1.7 degrees at A_s = +95 ^{o}C to a maximum of 6 degrees at A_s = -50 ^{o}C. The standard deviation of M_s varies from a minimum of 1.6 degrees at A_s = +95 ^{o}C to a maximum of 8 degrees at A_s = -50 ^{o}C. However, the standard deviation of As is smaller for most of the alloys.

Not withstanding the importance of A_f or M_f for functionality of a device, the A_s appears to be the most reliable measure of the raw material formulation. That is, if the A_s of a material varies from the mean by more than 3 standard deviations, then there is a very high probability that the material in question is not the correct alloy. Since the standard deviation of A_s is the smallest, the probability of accepting off-formulation material is minimized by specifying A_s.

CONCLUSIONS

- The reproducibility of transformation temperature parameters measured by differential scanning calorimetry (DSC) by a fixed practice on a small spool of wire is good.

- On a small spool of wire, the standard deviation of A_s in the solution annealed condition is 0.2 degrees for binary alloy formulated at A_s = -10°C.

- Thermal analysis results are very sensitive to the cooling rate of the sample from annealing for very small samples in the range of 40 milligrams.

- The standard deviation of transformation temperature parameter measured by DSC on a wide range of Ni – Ti binary alloys made by VIM – VAR varies by alloy formulation, by parameter and by product form.

- The variations in transformation temperature found in the VIM – VAR products may be attributed to variations in product chemistry. Further analytical work is needed on this topic.

- For the VIM – VAR product tested by a fixed practice, the dominant variable in determining the magnitude of standard deviation of the transformation temperature parameter is the alloy formulation.

- The A_s appears to be the most reliable measure of the raw material alloy formulation. That is, the standard deviation of A_s is the smallest. If A_s of a test sample varies from the target by more than 3 standard deviations of the target alloy, then there is a very high probability that the material in question is not the correct alloy formulation.

- Future specifications for Ni – Ti alloys should consider the variations in the standard deviations for the transformation temperature parameters. A single specification tolerance cannot be applied to all alloys and to all transformation parameters. A single tolerance may be too big for higher temperature alloys and too small for low temperature alloys.

REFERENCES

1. K. N. Melton, "Ni – Ti Based Shape Memory Alloys" in Engineering Aspects of Shape Memory Alloys", edited by Duerig et. al., London, 1990, pp 21-35.
2. Nishida, Wayman and Honma, Met. Trans, A, Vol 17A, 1986, pp 1505-1515.
3. Melton, ibid.
4. "Draft Standards for Nitinol Alloys Present Optimum Medical Device Design Processes", ASTM Standardization News, February, 2000, p 17.
5. Standard Test Method for Transformation Temperature of Nickel – Titanium Alloys by Thermal Analysis, ASTM F2004 – 00, ASTM, 100 BarrHarbor Drive, West Conshohocken, PA, 19428.