THE EFFECT OF ALLOY FORMULATION ON THE TRANSFORMATION TEMPERATURE RANGE OF Ni – Ti SHAPE MEMORY ALLOYS

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ABSTRACT

Thermal analysis data and statistics are presented on nine binary Ni – Ti alloys ranging from $A_s = +95^oC$ down to $A_s = -50^oC$. The material was made by vacuum induction melting (VIM) followed by vacuum arc remelting (VAR). The VIM pieces are bundled to make the electrodes for VAR. 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 deviation of the parameter increases as the alloy A_s decreases. Recommendations are made for alloy specifications.

KEYWORDS: Nickel – Titanium, Transformation Temperature, Differential Scanning Calorimetry, Statistics.

INTRODUCTION

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.

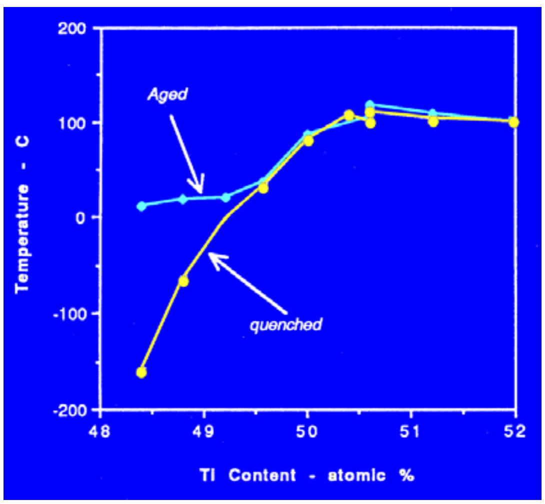


Figure 1. A_s temperature of Ni – Ti Alloys.

The relationship between chemistry and transformation temperature is complicated by precipitation of second phase in nickel rich alloys. Aging at temperatures below 800°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].

Setting aside the aging effects, the curve for fully solutioned alloys has significant implications for commercial alloy production. In a perfectly homogeneous product, transformation temperature would be perfectly uniform. Typical commercial products exhibit a range of transformation temperature. This implies that chemistry variation on the order of 0.1% by weight exists in large Ni –Ti ingots.

Consideration of the change in slope of the transformation temperature versus chemistry curve leads to the hypothesis that for constant variation in chemistry within ingots, 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.

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 or to specify the product.

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]. A 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, Special Metals did a series of ruggedness tests to assess the reproducibility of DSC. This data was used as a basis for evaluating the data from different production alloys.

PROCEDURES

All of the data in this analysis is taken from production ingots made at Special Metals from 1995 through 2003 by vacuum induction melting (VIM) followed by vacuum arc remelting (VAR). We describe this process as bundled VAR. That is the electrode for VAR is constructed from several pieces made by VIM. Bundling provides the opportunity to optimize the utilization of material from VIM by damping out the variability of the transformation temperature coming from the VIM process.

DSC is done on every VIM heat and at critical steps during processing. In 1995 individual VIM heats were 14 Kg and electrodes for VAR weighed 800 Kg. The re-melted ingots were 300 mm in diameter. In 2003, individual VIM heats weigh in excess of 180 Kg and VAR electrodes weigh in excess of 1600 Kg. Ingots are now 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 described above necessitate careful and consistent sample preparation for DSC. Special Metals has a fixed procedure for DSC which include sample preparation, heat treatment and calorimetry. Special Metals follows the ASTM standard test method in every respect except the heat treatment time for wire samples. Beginning in 1989, the procedure used for wire had a shorter heat treat time. To be consistent over time, we have not changed that heat treatment time.

We designate binary alloys by the A_s in the fully annealed condition. Nine alloys were evaluated between A_s = +95°C and A_s = -50 °C. These include A_s = +95 °C, +55 °C, +30 °C, +5 °C, 0 °C, -10 °C, -15 °C, -25 °C and A_s = -50 °C.

Each data set was reviewed for outlier data points. For example, large variations in transformation temperature can occur at the very 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 were calculated. 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 nine tests on one spool of wire weighing 4.5 Kg. One standard deviation on the A_s is 0.2 degrees. All of the standard deviations are less than one degree. The standard deviations on the other transformation temperature parameters increase as the parameter diverges from the A_s.

Table 1. Pre-Test of C7-7105-2A Redraw Wire

Sample	Weight (mg)	Mf °C	Mp °C	Ms °C	As °C	Ap °C	Af °C
Lead 1	42.4	-35.0	-25.4	-18.2	-6.3	3.5	7.4
Lead 2	35.9	-33.9	-24.3	-17.8	-6.4	3.1	6.5
Lead 3	39.4	-34.4	-24.7	-17.8	-6.1	3.5	7.0
Middle 1	39.5	-34.5	-24.7	-18.0	-6.7	2.7	6.4
Middle 2	41.6	-35.2	-25.3	-18.5	-6.6	2.9	6.5
Middle 3	36.2	-34.8	-25.1	-18.3	-6.2	3.3	6.7
Tail 1	37.3	-33.5	-24.2	-17.5	-6.4	3.0	6.4
Tail 2	41.5	-34.4	-24.6	-17.9	-6.5	3.0	6.6
Tail 3	39.5	-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

Table 2 shows the statistical analysis of the nine alloy data sets. The magnitude of the standard deviation varies by alloy and by transformation temperature parameter. The smallest data set contains 85 tests and the largest set contains 2429 tests. In 8 of the 9 the data sets, the As has the smallest standard deviation. Table 3 shows a breakdown of transformation temperature data by product form for the alloy at As = -25 ^{o}C. In this case VIM electrode data was included in the analysis for comparison to the VAR product.

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

Alloy As	Product Form	Heats	Tests		Mf oC	Mpeak oC	Ms oC	As oC	Apeak oC	Af oC
+95	All	19	272	Average	61.4	70.0	82.7	93.8	107.2	113.3
				STDEV	2.4	2.2	1.6	1.7	1.9	2.7
+55	All	4	85	Average	24.6	33.5	40.2	53.7	69.7	74.4
				STDEV	5.4	4.2	2.0	1.7	3.0	3.7
+30	Redraw	2	99	Average	1.0	9.7	16.6	29.5	42.7	49.8
				STDEV	8.4	6.5	3.4	2.1	4.0	3.9
+5	All	15	951	Average	-24.9	-14.9	-8.5	5.7	16.8	24.0
				STDEV	9.0	6.7	4.3	2.8	4.0	4.7
0	All	12	921	Average	-29.0	-18.9	-12.8	1.0	11.8	18.0
				STDEV	7.7	5.6	3.4	2.4	3.8	4.8
-10	All	48	1436	Average	-38.5	-27.9	-22.8	-9.4	0.4	5.8
				STDEV	9.0	6.5	4.3	2.8	3.2	5.2
-15	Bar	23	171	Average	-40.7	-29.1	-25.5	-16.0	-6.6	-0.5
				STDEV	3.9	3.2	3.9	2.6	2.5	4.4
-25	All	63	2429	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
-50	Bar, Coil	17	121	Average	-82.4	-67.6	-61.0	-51.8	-39.8	-31.1
				STDEV	8.1	6.3	8.0	6.0	4.7	5.4

Table 3. Standard Deviation of Transfomation Temperature for Various Product Forms at As = -25°C

Product Form	Sample Form	Number Heats	Number Tests		Mf	Mpeak	Ms	As	Apeak	Af
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 analysis was done on the data distributions for alloys at As = +95oC and As = -25oC. This is shown in Figures 2 and Figure 3 respectively. Figures 4, 5 and 6 show the effects of the number of heats, number of tests and the alloy formulation on the standard deviation of As, Af and Mf, respectively for wire for all of the alloys.

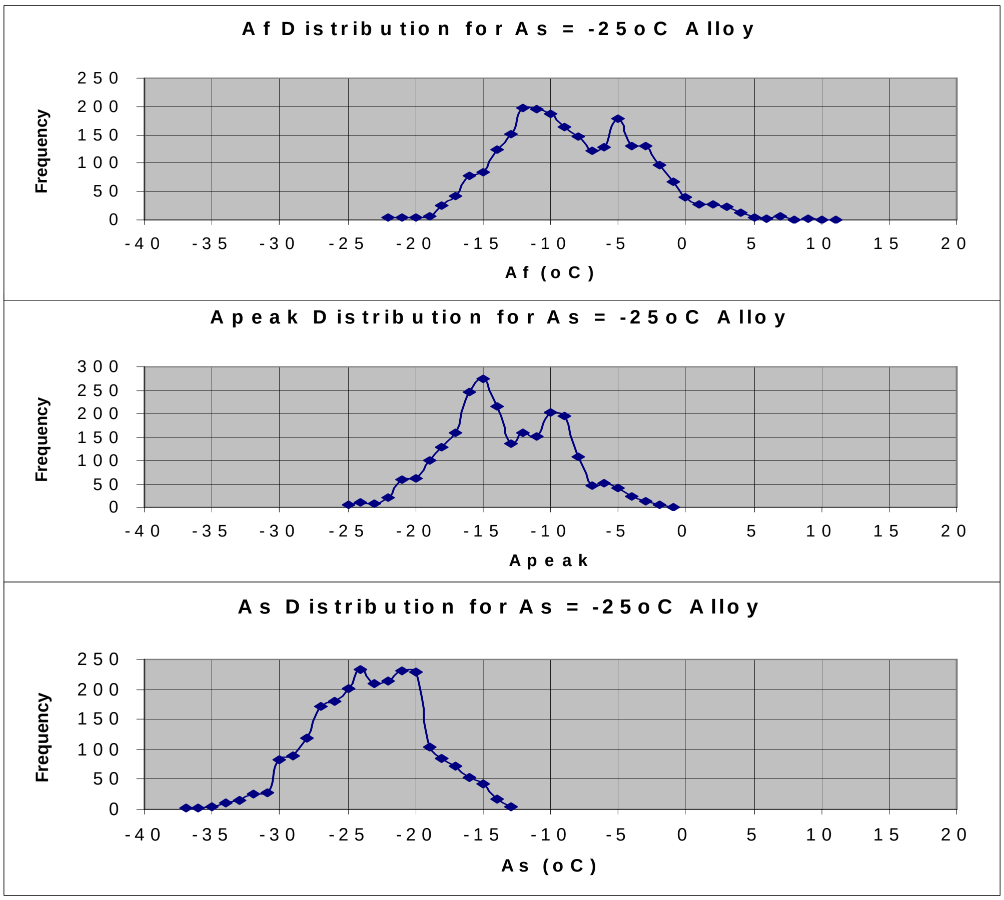


Figure 2. Distribution of Transformation Temperatures at A_s = -25°C

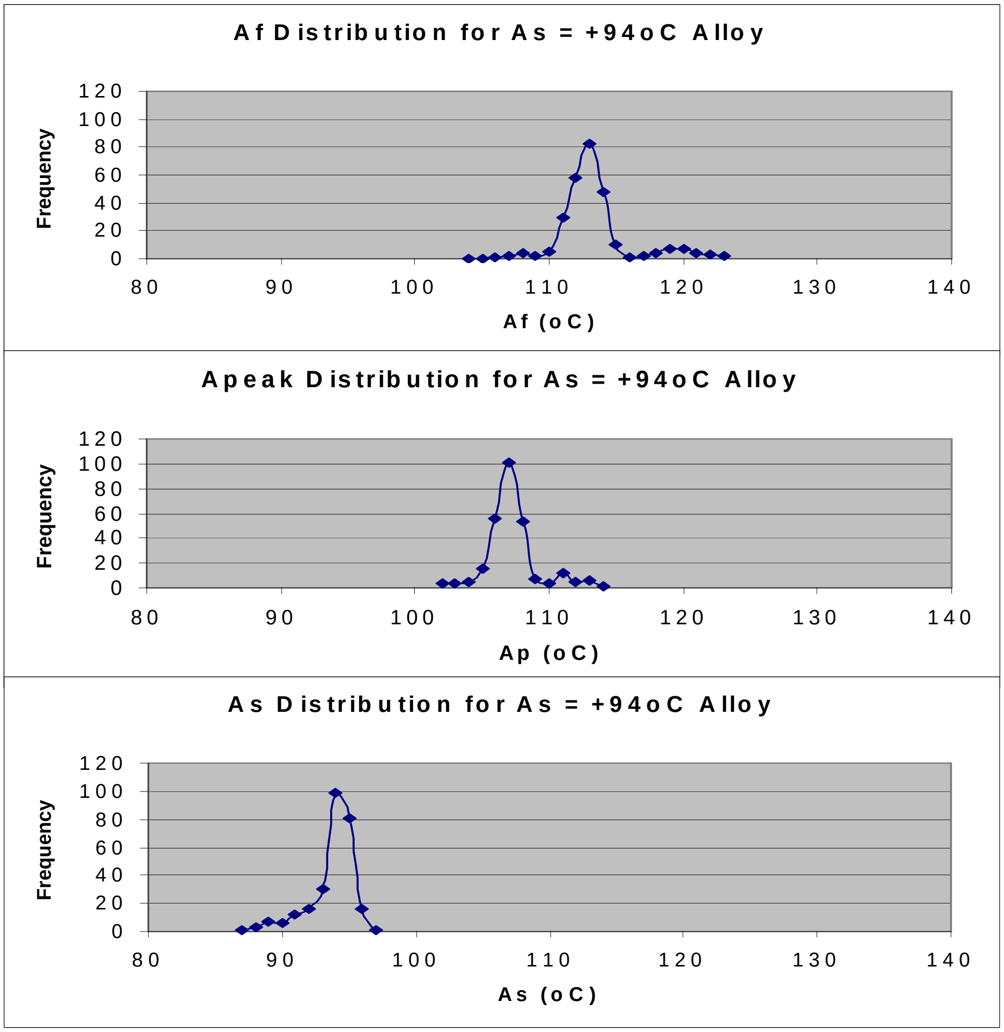
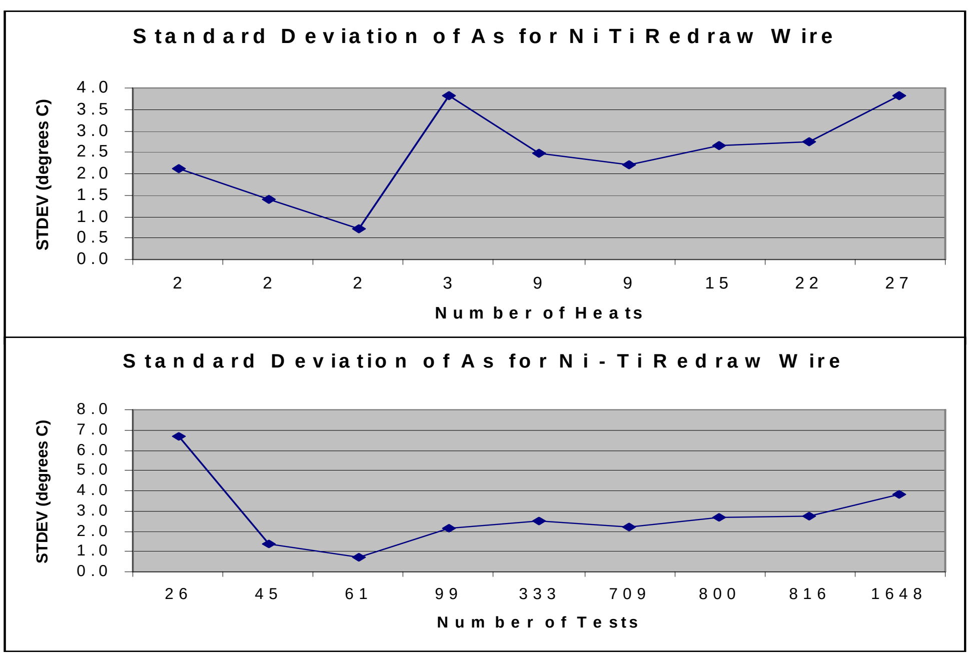


Figure 3. Distribution of Transformation Temperatures at $A_s = +95^oC$



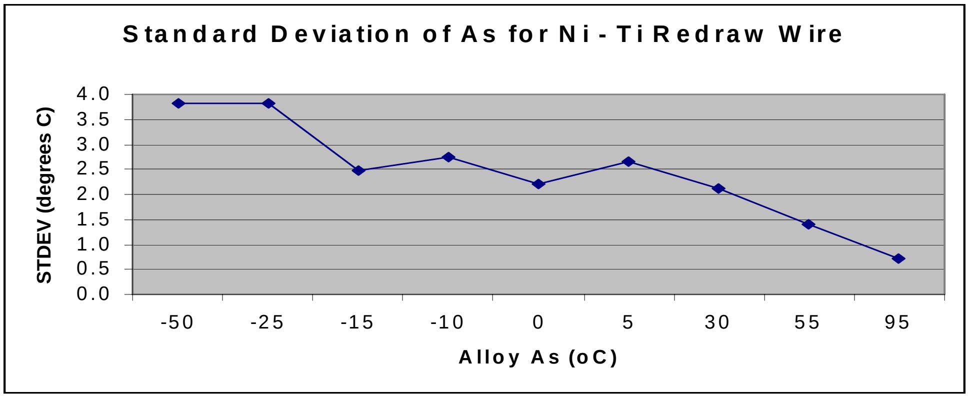


Figure 4. The Variation of the Standard deviation of As.

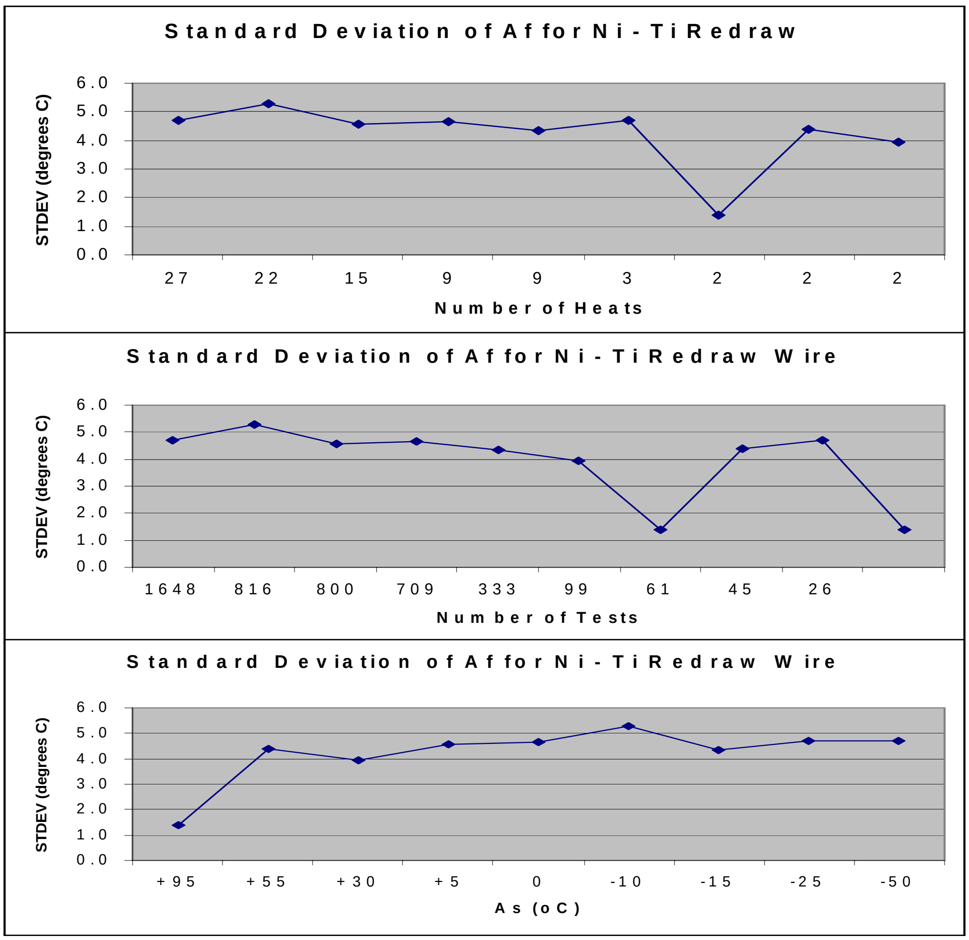


Figure 5. The Variation of the Standard deviation of Af.

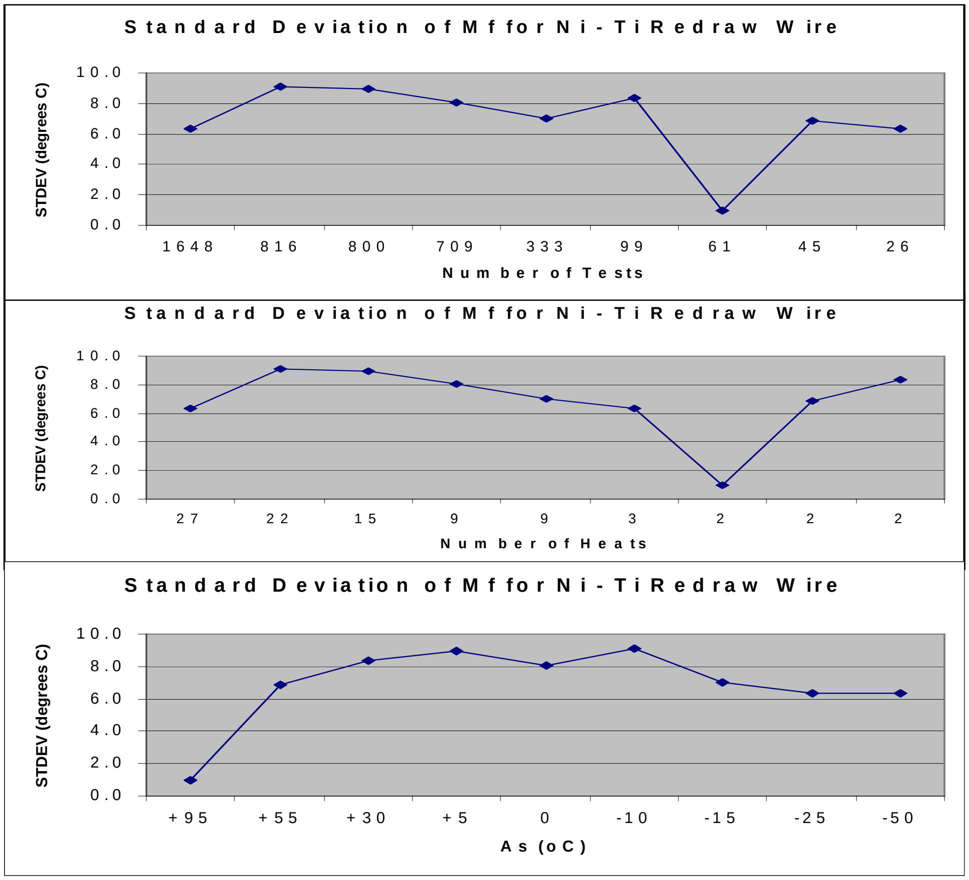


Figure 6. The Variation of the Standard deviation of Mf.

DISCUSSION

The ruggedness test data is a basis for evaluation of the data for the various alloys. This data indicates that test techniques and micro-segregation have a small effect on the range of transformation temperatures. All of the standard deviations obtained in alloy comparison are nominally one order of magnitude larger than those obtained in the ruggedness tests. Therefore the variations obtained in the alloy data may be attributed to variations in product chemistry.

In this analysis, the standard deviation of the transformation temperature varies by parameter, by alloy and by product form. The standard deviation of As varies from a minimum of 1.7 degrees at As = +95 ^{o}C to a maximum of 6 degrees at A_S = - 50 ^{o}C. There is also a small correlation to the number of heats and tests in the data set.

A comparison of the standard deviations from VIM and from VAR at As = -25oC confirms that bundling reduces the variability of the product. Table 3 also shows an increase in the average A_S at coil. This is consistent with other high Ni products. This may be the combined effect of residual aging in the hot rolled coil and a change in the sample form. VIM electrode and hot rolled 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.

The data distributions illustrated graphically at As = -25oc and at As = +95oC have some similarities and some differences. For both alloys, the As curves approaches a normal configuration but has a tail toward lower temperatures. For both alloys the Apeak and Af curves have tails 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 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.

Not withstanding the importance of Af or Mf for functionality, the A_s appears to be the most reliable measure of the raw material alloy 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 is good.

- On a small spool of wire, the standard deviation on A_s in the solution annealed condition is 0.2 degrees at A_s = -6^{o}C.

- 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, by product form and by the number of heats and tests for each alloy.

- 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, the dominant variable in determining the magnitude of standard deviations 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 As is the smallest. If A_s varies from the mean by more than 3 standard deviations, then there is a very high probability that the material in question is out of specification.

- Further statistical analysis may increase our understanding of the data.

- 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 broad for higher temperature alloys and too narrow for low temperature alloys.

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