Designation: F2004 – 05 (Reapproved 2010)

Standard Test Method for Transformation Temperature of Nickel-Titanium Alloys by Thermal Analysis[1]

This standard is issued under the fixed designation F2004; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method defines procedures for determining the transformation temperatures of nickel-titanium shape memory alloys.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E473 Terminology Relating to Thermal Analysis and Rheology

E967 Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers

E1142 Terminology Relating to Thermophysical Properties

F2005 Terminology for Nickel-Titanium Shape Memory Alloys

3. Terminology

3.1 Specific technical terms used in this test method are found in Terminologies E473, E1142, and F2005.

4. Summary of Test Method

4.1 This test method involves heating and cooling a test specimen at a controlled rate in a controlled environment through the temperature interval of the phase transformation. The difference in heat flow between the test material and a reference material due to energy changes is continuously monitored and recorded. Absorption of energy due to a phase transformation in the specimen results in an endothermic peak on heating. Release of energy due to a phase transformation in the specimen results in an exothermic peak on cooling.

5. Significance and Use

5.1 Differential scanning calorimetry provides a rapid method for determining the transformation temperature(s) of nickel-titanium shape memory alloys.

5.2 This test method uses small, stress-free, annealed samples to determine whether a sample of nickel-titanium alloy containing nominally 54.5 to 56.5 % nickel by weight is austenitic or martensitic at a particular temperature. Since chemical analysis of these alloys does not have sufficient precision to determine the transformation temperature by measuring the nickel to titanium ratio of the alloy, direct measurement of the transformation temperature of an annealed sample of known thermal history is recommended.

5.3 This test method is useful for quality control, specification acceptance, and research.

5.4 Transformation temperatures derived from differential scanning calorimetry (DSC) may not agree with those obtained by other test methods due to the effects of strain and load on the transformation.

6. Interferences

6.1 Make sure the material to be tested is homogeneous since milligram sample quantities are used.

6.2 Take care in preparing the sample. Cutting and grinding can cause cold work, which affects the transformation temperature. Oxidation during heat treatment can change the thermal conductance of the sample.

6.3 Set the gas flow to provide adequate thermal conductivity in the test cell.

7. Apparatus

7.1 Use a differential scanning calorimeter capable of heating and cooling at rates up to 10°C/min and of automatically

[1] This test method is under the jurisdiction of ASTM Committee F04 on Medical and Surgical Materials and Devices and is the direct responsibility of Subcommittee F04.15 on Material Test Methods.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

recording the differential energy input between the specimen and the reference to the required sensitivity and precision.

7.2 Use sample capsules or pans composed of aluminum or other inert material of high thermal conductivity.

7.3 Use helium gas purge supply. See 10.3.1.

7.4 Use an analytical balance with a capacity of 100 mg capable of weighing to the nearest 0.1 mg.

8. Sampling

8.1 Use a sample size of 25 to 45 mg. Cut the sample to maximize surface contact with the (DSC) sample pan.

8.2 Anneal the sample at 800 to 850°C for 15 to 60 min in vacuum or inert atmosphere, or in air with adequate protection from oxidation. Rapidly cool the sample to prevent precipitation of phases which may change transformation temperature of the alloy.

8.3 Clean the sample of all foreign materials such as cutting fluid. If the sample is oxidized in heat treatment, grind, polish, or etch the sample to remove the oxide. Take care to avoid cold working the sample as this will change its thermal response. Slight oxidation is permissible but remove all heavy oxide scale.

9. Calibration

9.1 Calibrate the temperature axis of the instrument using the same heating rate, purge gas, and flow rate as those used for analyzing the specimen in accordance with Practice E967.

10. Procedure

10.1 Place the sample on the sample pan and place the pan on the test pedestal.

10.2 Place an empty pan on the reference pedestal.

10.3 Turn on the purge gas at a flow rate of 10 to 50 mL/min.

10.3.1 Use helium as the purge gas for the sample chamber.

10.3.2 Use a dry air, helium, or nitrogen cover gas. The dry gas shall have a dew point below the lowest temperature of the cooling cycle.

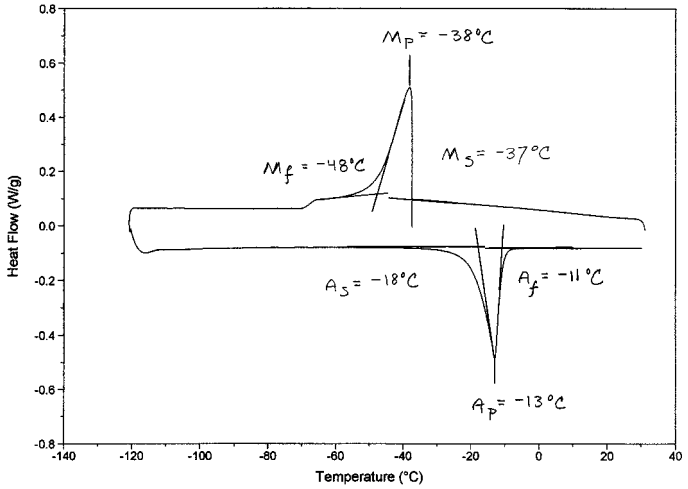

FIG. 1 DSC Curve for Nickel-Titanium (NiTi)

10.4 Run the cooling and heating program.

10.4.1 Use the heating and cooling rates of 10 ± 0.5°C/min.

10.4.2 Heat the sample from room temperature to a temperature of at least A_f + 30°C; hold at temperature for a time sufficient to equilibrate the sample with the furnace.

10.4.3 Cool the sample to a temperature of below M_f – 30°C; hold for a time sufficient to equilibrate the sample with the furnace. Then, heat the sample to a temperature of at least A_f + 30°C.

10.5 *Data Acquisition*—Record the resulting curve from the heating and cooling program from A_f + 30°C to M_f – 30°C.

11. Graphical Data Reduction

11.1 Draw the baselines for the cooling and heating portions of the curve as shown in Fig. 1.

11.2 Draw the tangents to the cooling and heating spikes through the inflection points as shown in Fig. 1. If a computer program is used to construct the tangents, care must be taken in locating the tangent points.

11.3 Obtain M_s, M_f, A_s, and A_f as the graphical intersection of the baseline with the extension of the line of maximum inclination of the appropriate peak of the curve as shown in Fig. 1. A_p is the peak minimum of the endothermic curve, and M_p is the peak maximum of the exothermic curve. Read A_p and M_p directly from the graph as shown in Fig. 1.

12. Report

12.1 Report the following information with the test results:

12.1.1 Complete identification and description of the material tested including the specification and lot number.

12.1.2 Description of the instrument used for the test.

12.1.3 Statement of mass, dimensions, and geometry.

12.1.4 Material for the specimen pan and temperature program.

12.1.5 Description of the temperature calibration procedure.

12.1.6 Identification of the specimen environment by gas, flow rate, purity and composition.

12.1.7 Results of the transformation measurements using the nomenclature in accordance with Terminology F2005. Temperature results should be reported to the nearest 1°C.

13. Precision and Bias

13.1 An interlaboratory study was conducted in accordance with Practice E691 in seven laboratories with three different materials, with each laboratory obtaining five results for each material. There were two rounds of testing. In the first round, all the test samples were annealed in one laboratory; in the second round, the samples were annealed by the laboratory that conducted the test. The details are given in ASTM Research Report No. F04–1008.[3]

13.2 The results of round one are summarized in Tables 1-6 for each transformation temperature parameter (M_f, M_p, M_s, A_s, A_p, A_f). The values are in degrees Celsius. The terms

[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:F04-1008.

TABLE 1 Precision of M_f

Material	M_f, grand mean	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
A	-50.0	0.57	3.97	1.6	11.1
B	-26.3	0.95	2.62	2.7	7.3
C	48.5	1.02	1.54	3.0	4.3

TABLE 2 Precision of M_p

Material	M_p, grand mean	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
A	-43.8	0.42	2.65	1.2	7.4
B	-20.5	1.10	2.21	3.1	6.2
C	58.1	0.88	1.05	2.5	2.9

TABLE 3 Precision of M_s

Material	M_s, grand mean	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
A	-41.6	0.40	2.35	1.1	6.6
B	-16.9	0.95	1.24	2.7	3.5
C	64.8	0.74	1.15	2.1	3.2

TABLE 4 Precision of A_s

Material	A_s, grand mean	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
A	-25.3	0.30	1.85	0.8	5.2
B	-4.8	0.32	1.58	0.9	4.4
C	72.9	0.65	2.68	1.8	7.5

TABLE 5 Precision of A_p

Material	A_p, grand mean	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
A	-19.4	0.16	1.94	0.5	5.4
B	5.7	0.57	1.50	1.6	4.2
C	94.7	0.85	3.18	2.4	8.9

TABLE 6 Precision of A_f

Material	A_f, grand mean	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
A	-23.4	0.23	2.01	0.6	5.6
B	2.5	0.67	1.39	1.9	3.9
C	91.6	0.80	2.25	2.2	6.3

repeatability limit and reproducibility limit are used as specified in Practice E177.

13.3 The results of round two are summarized in Tables 7-12 for each transformation temperature parameter (M_f, M_p, M_s, A_s, A_p, A_f). The values are in degrees Celsius. The terms repeatability limit and reproducibility limit are used as specified in Practice E177.

TABLE 7 Precision of M_f, When Samples are Annealed by Testing Laboratory

Material	M_f, grand mean	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
A	-49.1	2.03	8.49	5.7	23.8
B	-27.3	1.85	5.93	5.2	16.6
C	48.5	1.23	1.84	3.4	5.1

TABLE 8 Precision of M_p, When Samples are Annealed by Testing Laboratory

Material	M_p, grand mean	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
A	-43.0	1.31	8.69	3.7	24.3
B	-21.5	1.67	7.31	4.7	20.5
C	58.1	1.31	1.47	3.7	4.1

TABLE 9 Precision of M_s, When Samples are Annealed by Testing Laboratory

Material	M_s, grand mean	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
A	-40.7	2.84	8.29	7.9	23.2
B	-18.9	2.38	6.60	6.7	18.5
C	64.8	1.39	2.29	3.9	6.4

TABLE 10 Precision of A_s, When Samples are Annealed by Testing Laboratory

Material	A_s, grand mean	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
A	-23.2	0.94	5.26	2.6	14.7
B	-4.1	0.52	1.93	1.4	5.4
C	72.9	0.70	2.80	2.0	7.8

TABLE 11 Precision of A_p, When Samples are Annealed by Testing Laboratory

Material	A_p, grand mean	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
A	-19.1	0.56	5.30	1.6	14.8
B	2.2	0.65	2.71	1.8	7.6
C	89.5	1.01	3.37	2.8	9.4

TABLE 12 Precision of A_f, When Samples are Annealed by Testing Laboratory

Material	A_f, grand mean	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
A	-16.6	0.87	4.95	2.4	13.9
B	6.6	0.69	4.07	1.9	11.4
C	94.7	0.91	2.61	2.5	7.3

14. Keywords

14.1 differential scanning calorimeter; DSC; nickel-titanium alloy; NiTi; Nitinol; shape memory alloy; TiNi; transformation temperature

APPENDIX

(Nonmandatory Information)

X1. RATIONALE

X1.1 This test method uses small, stress-free, annealed samples to determine whether a sample of nickel-titanium alloy containing nominally 54.5 to 56.5 % nickel by weight is austenitic or martensitic at a particular temperature. Since chemical analysis of these alloys does not have sufficient precision to determine the transformation temperature by measuring the nickel to titanium ratio of the alloy, direct measurement of the transformation temperature of an annealed sample of known thermal history is recommended.

X1.2 It is well known that slow cooling after annealing of nickel-rich alloys allows precipitates of the Ni_4Ti_3 type to form, thereby increasing the Ti content of the matrix and the transformation temperatures. The practice is to avoid slow cooling preserve the "as annealed" transformation. It is possible, however, to cool the samples too quickly, raising the transformation temperature, possibly due to stress effects which retain residual martensite. One method of achieving the desired cooling rate is to heat treat the test specimens on a foil tray and then allow the samples and the foil tray to cool together, out of the furnace, in room temperature air.

X1.3 Transformation temperatures derived from differential scanning calorimetry (DSC) may not agree with those obtained by other test methods due to the effects of strain and load on the transformation.

X1.4 Differences in sample preparation techniques between laboratories influenced the reproducibility limit. Differences in calibration techniques may have also influenced reproducibility. To minimize interlaboratory variations in results, common sample preparation and calibration practices must be established.