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Evaluation of TGA as a Quality Assurance Tool for Surface Modified Zircoloy-4

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Evaluation of TGA as a QA tool for Surface Modified Zircoloy-4

Executive Summary

Thermogravimetric analysis (TGA) and coupled Mass Spectroscopy (MS) were evaluated to determine their suitability as a quality assurance tool for surface modified nickel plated zircoloy-4 liner tubes. Samples with 0, 0.1, 0.2, 0.3, and 0.4 mils of heat treated nickel plate were tested at 330, 370, and 400°C. Not all of the samples exhibited the expected typical parabolic shaped oxidation curve. The measured weight change was consistent for the as received and 0.2 mil and the 0.4 mil surface modified samples. None of the samples were tested under aggressive enough conditions to consume the surface modified materials during the test duration. Use of the Mass Spectrometer in conjunction with the TGA did not produce valuable data and was only used for the 400°C test series; however, the TGA was valuable. The 0.1 and 0.3 mil surface modified Zr-4 samples exhibited thru surface modified layer cracks which could account for the variation in oxidation behavior. TGA tests for periods up to six hours appear viable as a method to ascertain oxidation behavior for consistent results. Additional testing of samples with known variations in surface modified layer thickness and quality is recommended as part of the QA acceptance testing.

Background

The Tritium Readiness (TR) Campaign is conducting a Development and Testing (D&T) Program to address several concerns that have arisen during the production of tritium in the commercial light water reactor (CLWR) program. One concern is the presence and cracking of water on the liner and spacers. These components are fabricated from Zircoloy-4 (Zr-4), an alloy developed for improved oxidation resistance compared to Zircoloy-2 or pure zirconium. A project was initiated to increase the oxidation rate of the liners and spacers, known as TPBAR Materials Ex-reactor Testing project 1 (TMED-1), Ref. 1. This task consisted of alloy development, surface modification, and archive alloy testing. Savannah River National Laboratory (SRNL) was tasked with determining the suitability of using thermogravimetric analysis (TGA) as a quality assurance tool for surface modified Zr-4. The intent of this testing is to supplant long term isothermal oxidation testing with the TGA to determine the oxidation characteristics in a four to six hour test.

Surface modification for this project consists of electroplating between 0.1 and 0.4 mils (0.0001 to 0.0004 inch) of nickel that is subsequently heat treated to form a series of nickel enriched zirconium intermetallic compounds. The composition of the surface modified layers depends on the heat treatment and the initial nickel thickness. The surface modification technology was developed by Pacific Northwest National Laboratory (PNNL) in conjunction with Sandia National Laboratories – California (SNL-CA).

Experimental

Liners from typical TPBAR stock were provided by PNNL to SRNL. The typical geometry of a liner is a 14 inch long tube with an outer diameter of approximately 0.18 inch and a wall thickness of 0.004 inch. These liners were provided in five conditions: As fabricated, and liners with 0.1 mil Ni, 0.2 mil Ni, 0.3 mil Ni, and 0.4 mil Ni plating. All the nickel plated samples were heat treated at PNNL prior to receipt. The heat treatment is 10°C/min to 750°C for 2 hours with a 10°C/min cool in argon. Only the external surfaces are surface modified (SM); the reported areas for the SM samples include only the external surface, whereas, the bare sample includes both internal and external surfaces.

The sample liners, shown in Figure 1, were cut using an electrical discharge machine (EDM) to approximately 1 inch lengths giving a starting mass of nominally 300 mg for an as received tube. Notches for hanging from a quartz rod were also incorporated into the samples, Figure 2. The samples were weighed in a Mettler Toledo balance to establish the appropriate counter weights for the TGA.

A simple gas manifold was assembled to control the moisture content of the reacting gas. A cylinder of research grade helium (99.99) was used. The gas stream was split and then mixed using two low flow rotameters. The gases were balanced to achieve a dew point of 2-6°C which is consistent with a pressure range of 7 – 9 Pa. The dew point of the deuterium oxide (heavy water with a purity of 99.96%) was controlled by setting the chiller temperature to 8°C and modulating the gas stream flows, Figure 3. After loading the sample in the Setaram SetSys TGA, Figure 4, the air was displaced from the chamber by flowing the gas for sixty minutes. The temperature was then increased at a rate of 20°C/min to the test temperature of 330, 370, or 400. The data logging frequency was determined by the TGA data acquisition program. Tests were run for 3, 16, and 20 hours. One test at 370°C was run for 72 hours.

Initially, the purge gas used was argon and the mass spectrometer (MS) was used to determine if there was any reduction in the heavy water signature during oxidation exposure. MS tests were conducted at 400°C. Upon examination of the data it was determined that this information did not provide additional value and no further tests were conducted with the MS. The carrier gas for the heavy water was subsequently changed to He.

Select samples, in both the as received and oxidized conditions, were examined using optical metallography. The microstructures were examined in the as polished condition.

All of the samples oxidized at 400°C were off gassed in argon during a temperature ramp to 900°C to see if there was any release of the nascent deuterium. The TGA and MS were used for this test. The MS was not calibrated to determine the amount of deuterium released.

Results and Discussion

The coupled TGA – MS data for the SM Zr-4 samples are shown in Figures 5-8 for the 0.1, 0.2, 0.3, and 0.4 mil thick nickel plated Zr-4 samples oxidized at 400°C, respectively. In considering the data from these oxidation exposures, it is not apparent that there is a relationship between the reacting gas and the weight gain. The D_2O exhibits anything from no change on heating and reacting to a constantly increasing signature. An examination of the AMU, for D_2 and He shows an increase in the relative amount but it does not exhibit similarities to the weight gain data. The comparative data for these samples are shown in Figure 9. Note that the 0.1 SM Zr-4 exhibits an anomalously large mass increase that is inconsistent with the thicker plated samples. The 0.2, 0.3, and 0.4 mil SM Zr-4 samples exhibit rapid initial oxidation rates that plateau to more consistent oxidation rates. These rates have not reached a slope comparable to as-received Zr-4 during the oxidation test duration used, as seen in Figure 10.

The oxidation data from samples tested at 370°C are presented in Figure 11. Four of the five samples tested exhibited the expected behavior with a fairly rapid initial oxidation rate, followed by a reduced rate. The expectation is that the rate will be further reduced to that consistent with the as-received Zr-4. This behavior was not observed due to the relatively short oxidation tests that were run compared to the data presented by W. Lusher (2). The 0.1 mil SM Zr-4 sample exhibits a sigmoidal oxidation curve rather than the parabolic oxidation curve that is expected for production of a compact adherent oxide layer (3, 4).

The oxidation data from samples tested at 330°C are presented in Figure 12. These samples exhibit the expected results for the as-received Zr-4 and the 0.2 and 0.4 mil Ni SM Zr-4 samples. These materials exhibit a large initial increase in mass followed by a reduced oxidation rate with time. The 0.1 and 0.3 mil SM Zr-4 samples exhibit a small increase with an increasing oxidation rate with time. The oxidation weight gain is significantly higher for the SM Zr-4 samples than for the as-received Zr-4.

The data were also plotted as a function of original nickel plating thickness. As shown in Figure 13, the as-received Zr-4 samples exhibit the expected behavior with a rapid transient oxidation rate followed by a slower rate. The odd oxidation behavior of the 0.1 mil thick SM Zr-4 is still apparent, although the low temperature behavior is a little different even than the higher temperature behavior, Figure 14. As shown in Figure 15, the oxidation behavior of the 0.2 mil SM Zr-4 is somewhat inconsistent with increasing test temperature. It appears that the total mass gain for the 370°C test will exceed the 400°C test sample; this behavior may be due to axial variation along the sample. Figure 16 shows the oxidation data for the 0.3 mil Ni SM Zr-4 sample and the weight gain data for the higher temperatures are consistent with expectations, both having an initial transient oxidation followed by a slower steady state rate. The 330°C sample did not exhibit the initial transient oxidation; rather it has an increasing rate with increasing time for the test duration. The oxidation data for the 0.4 mil Ni SM Zr-4 sample are shown in Figure 17. The oxidation behavior of this sample is the most consistent with expectations with a transient oxidation period followed by the steady period. The 330°C test has a slight inflection near the beginning of the test but this apparent anomaly was altered and the oxidation curve appeared more or less as expected after this point. Unlike the long term tests

that were conducted at SNL and PNNL, these tests considered the initial transient oxidation whereas the tests from SNL and PNNL considered steady state oxidation and often did not have data for time periods less than one day.

Metallographic examination was conducted on several of the samples to determine whether there were obvious reasons for the unexpected behavior. The as received and oxidized conditions for the 0.1 mil SM Zr-4 are shown in Figure 18a and 18b. These images show a large number of cracks in the nickel plating after oxidation. It is possible that these cracks can help explain the increased oxidation rate by increasing the effective surface area. There were fewer cracks visible in the 0.2 mil SM Zr-4 and some in the 0.3 SM Zr-4. The presence of the cracks and the associated apparent increased oxidation rate may not be detrimental for the TPBARs provided the component retains the needed structural integrity.

The oxidation weight gain relative to PNNL data from plate samples, which were tested at comparable temperatures for 30 days, is presented in Table 2. The relative duration of the tests (TGA test duration vs. 30 day PNNL static test duration) is also shown in the table. These data indicate that at times as short as 2% of comparison data, the surface modified liners tested in the TGA gained up to 12% of the total mass gained by the flat coupon samples tested by PNNL (Ref 2.). These results can be interpreted in several different ways. The first is that the initial oxidation rates for the liner samples (TGA) are significantly higher than the longer term oxidation rates. A second possibility is that the liner oxidation properties are different than those of the plate oxidation samples that PNNL tested.

Dedeuteriding

The MS / TGA data for the dedeuteriding tests are shown in Figures 19-25 and at higher resolution for AMU 4 ($^2H_2$) in Figures 26-32. The weight gain data for the samples are summarized in Table 3. Note that the samples all exhibited significant weight gains despite being run in dry argon; two 0.1 mil Ni SM Zr-4 samples, oxidized and as-received, were examined using XRD to determine the predominant reaction products. The results are shown in Figures 35 and 36. The XRD data were taken from portions of the samples that were crushed in preparation for the testing. These data do not reveal any species that are not expected. The oxide and nitride have similar diffraction patterns and are difficult to separate. Based on the MS data and the low oxygen levels, one would not expect gross oxides on the as received, not previously oxidized sample. It is interesting to note, that after the 900°C excursion many of the samples broke in the EDM hanger area on cooling.

The baseline gas characteristics can be seen in Figure 33 for a blank sample. The MS current data, which is an indication of pressure, shows that the baseline current for the blank is about $4.6x10^{-13}$A and is reasonably flat for the thermal excursion. This information can be used to develop semi-quantitative estimates of the deuterium that was evolved during heating. As stated previously, no calibration of the instrument to truly quantitative work was conducted. However, the relative amplitudes for deuterium, water, and nitrogen are listed in Table 3. The water peaks are fairly consistent across all the samples, including the blank. This suggests that moisture is

being evolved from surfaces within the TGA column, although there could be some contribution from adsorbed O^2H (deuterium hydroxide).

The total deuterium pick-up, based on Zr^2H_2 formation, can be estimated from the oxidation weight gain and assuming that this weight gain is due to 100% cracking of the D_2O and subsequent formation of oxide and deuteride in the sample. These data are listed in Table 4 and show that the 0.1 mil Ni SM Zr-4 sample could have a maximum amount of 1.37 mg of deuterium, with other samples exhibiting less total mass gain attributable to deuterium. The relative deuterium peak heights from the mass spectrometer, Table 3, indicate that the weight gain in heavy water is in qualitative agreement. In addition, the areas under the peaks were estimated by numerically integrating the current and time. These data are presented in Table 4 and also show qualitative agreement with the weight gains. The weight gain on heating to 900°C is much larger than the weight loss due to the deuteride decomposition, thus the weight difference is difficult to quantify. Additional testing of multiple samples and calibrated gas compositions could be used to improve the quantitative nature of these results.

Conclusions

Due to the sample size, the equipment configuration and the required gas flow rates, coupled TGA / MS did not reveal any decrease in the heavy water signature during oxidation.

TGA is a useful tool for determining the initial oxidation behavior of the surface modified Zr-4 material. The TGA data exhibits a number of characteristic weight gains that are consistent for oxidizing materials that form compact dense oxide layers and for materials that do not.

The oxidation data for the 0.1 SM Zr-4 and several sections of the 0.3 SM Zr-4 material indicates that these materials are not forming dense oxide layers. Metallographic examination of samples in the as received and oxidized conditions indicate that the tubing may exhibit numerous microcracks that would increase the apparent surface area and could account for the more rapid than expected oxidation rates.

TGA tests at 400°C for a minimum duration of 5 hours appear to be sufficient to separate expected behavior from anomalous behavior. Tests of this duration, while longer than typically desired for QA tests are significantly shorter than the multi-day tests required for typical furnace tests.

Samples oxidized in heavy water crack the water and create nascent deuterium. It is expected that this material is present as a deuteride, (Zr^2H_2) that decomposes at temperatures in excess of 600°C. The relative amounts of deuterium, based on numeric integration of the MS peaks, are consistent with the total weight gain during oxidation, although truly quantitative results were not obtained during this study.

Acknowledgements

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References

1. TTP-3-033, Rev. 0, Test Plan for Ex-Reactor Liner Oxidation Experiment (TMED-1), Tritium Technology Program, D.J. Senor, PNNL, 11 April, 2008.

2. 50% Design Review – Surface Modified Lower Cruciforms, Walter Luscher, Ph.D. August 2008

3. C. Wagner, Z. Phys. Chem., B21, 25, 1933

4. N. Birks and G. H. Meier, Introduction to High Temperature Oxidation of Metals, Arnold, Baltimore, 1983.

Table 1. Test conditions for bare and SM Zr-4

Sample Identification	Temp (°C)	Dew Point (°C)	Mass (mg)	Length (in)	Dia (in)	Area (cm^2)
TMED1a	400	-4.0	263.1	1.107	0.205	4.588
TMED11	370	3.2	272.1	1.098	0.205	4.562
TMED12	330	3.4	269.1	1.096	0.205	4.554
TMED2a	400	1.0	287.8	1.103	0.206	4.605
TMED21	370	2.7	281.6	1.097	0.206	4.580
TMED22	330	5.2	281.9	1.095	0.206	4.572
TMED3a	400	1.8	296.0	1.101	0.210	4.686
TMED31	370	2.8	299.1	1.107	0.210	4.712
TMED32	330	5.6	297.8	1.104	0.210	4.699
TMED4b2	400	-1.5	300.5	1.103	0.211	4.717
TMED42	370	3.9	306.4	1.103	0.211	4.717
TMED43	330	2.2	291.8	1.046	0.211	4.473
AS1*	400	6.7	280.8	1.097	0.204	8.894
AS2*	370	2.5	281.0	1.095	0.204	8.878
AS3*	330	1.8	271.9	1.093	0.204	8.861

* Both internal and external surfaces are included for the bare while only external surfaces were considered for the SM materials.

Table 2. Fractional weight gain of the liner samples compared to the plate sample data in Ref. 2 based on a linear oxidation rate.

Time	Life	% of total weight gain at 330°C				% of total weight gain at 370°C				
(min)	(%)	0.1 Ni	0.2 Ni	0.3 Ni	0.4 Ni	AR Zr-4	0.1 Ni	0.2 Ni	0.3 Ni	0.4 Ni
180	0.42	1.06	2.60	1.49	3.16	2.15	4.47	9.46	4.19	5.95
360	0.83	1.86	4.68	3.47	4.55	3.34	12.25	13.11	7.02	7.32
720	1.67	4.24	7.71	8.42	5.44	4.62	NA	NA	NA	NA
959	2.22	6.50	9.36	11.14	5.81	5.10	NA	NA	NA	NA

Table 3. Baseline mass spectrometer current for D2, H2O and N2.

Sample	D_2 x 10^{-13} (A)		H_2O x 10^{-12} (A)		N_2 x 10^{-13} (A)
	Baseline	Peak	Baseline	Peak	Baseline
Blank	4.72	4.74	8.16	9.65	19.1
Zr-4 – Ox	4.69	4.83	7.69	9.05	7.72
Zr-4 + 0.1 Ni – Ox	4.88	17.3	11	19.9	7.65
Zr-4 + 0.2 Ni – Ox	5.01	5.10	5.73	8.96	3.33
Zr-4 + 0.3 Ni – Ox	4.89	6.06	8.92	11.6	11.2
Zr-4 + 0.4 Ni – Ox	4.75	5.93	10.5	13.5	9.06
Zr-4 + 0.1 Ni (As Rec'd)	4.70	4.71	7.41	9.87	9.05

Table 4. Oxidation weight gain, integrated area (AMU 4), and dehydride weight gain

Sample	Mass attributable to D_2O cracking	Integrated area (A*s) X 10^{-10}	Weight gain in Ar (mg)
Zr-4 – Ox	0.174	0.274	12.30
Zr-4 + 0.1 Ni – Ox	1.37	15.1	10.88
Zr-4 + 0.2 Ni – Ox	0.346	0.195	13.69
Zr-4 + 0.3 Ni – Ox	0.740	2.20	11.19
Zr-4 + 0.4 Ni – Ox	0.686	1.96	11.46
Zr-4 + 0.1 Ni (As Rec'd)	0	0	12.60
Zr-4 + 0.1 Ni (As Rec'd – N_2 Test)	0	0	0.156

Table 5. Test conditions for bare and SM Zr-4

Sample Identification	Temp (°C)	Dew Point (°C)	Mass (mg)	Length (in)	Dia (in)	Area (cm^2)
TMED1a	400	-4.0	263.1	1.107	0.205	4.588
TMED11	370	3.2	272.1	1.098	0.205	4.562
TMED12	330	3.4	269.1	1.096	0.205	4.554
TMED2a	400	1.0	287.8	1.103	0.206	4.605
TMED21	370	2.7	281.6	1.097	0.206	4.580
TMED22	330	5.2	281.9	1.095	0.206	4.572
TMED3a	400	1.8	296.0	1.101	0.210	4.686
TMED31	370	2.8	299.1	1.107	0.210	4.712
TMED32	330	5.6	297.8	1.104	0.210	4.699
TMED4b2	400	-1.5	300.5	1.103	0.211	4.717
TMED42	370	3.9	306.4	1.103	0.211	4.717

TMED43	330	2.2	291.8	1.046	0.211	4.473
AS1*	400	6.7	280.8	1.097	0.204	8.894
AS2*	370	2.5	281.0	1.095	0.204	8.878
AS3*	330	1.8	271.9	1.093	0.204	8.861

* Both internal and external surfaces are included for the bare while only external surfaces were considered for the SM materials.

Table 6. Fractional weight gain of the liner samples compared to the plate sample data in Ref. 2 based on a linear oxidation rate.

Time	Life	% of total weight gain at 330°C				% of total weight gain at 370°C				
(min)	(%)	0.1 Ni	0.2 Ni	0.3 Ni	0.4 Ni	AR Zr-4	0.1 Ni	0.2 Ni	0.3 Ni	0.4 Ni
180	0.42	1.06	2.60	1.49	3.16	2.15	4.47	9.46	4.19	5.95
360	0.83	1.86	4.68	3.47	4.55	3.34	12.25	13.11	7.02	7.32
720	1.67	4.24	7.71	8.42	5.44	4.62	NA	NA	NA	NA
959	2.22	6.50	9.36	11.14	5.81	5.10	NA	NA	NA	NA

Table 7. Baseline mass spectrometer current for D2, H2O and N2.

Sample	D_2 x 10^{-13} (A)		H_2O x 10^{-12} (A)		N_2 x 10^{-13} (A)
	Baseline	Peak	Baseline	Peak	Baseline
Blank	4.72	4.74	8.16	9.65	19.1
Zr-4 – Ox	4.69	4.83	7.69	9.05	7.72
Zr-4 + 0.1 Ni – Ox	4.88	17.3	11	19.9	7.65
Zr-4 + 0.2 Ni – Ox	5.01	5.10	5.73	8.96	3.33
Zr-4 + 0.3 Ni – Ox	4.89	6.06	8.92	11.6	11.2
Zr-4 + 0.4 Ni – Ox	4.75	5.93	10.5	13.5	9.06
Zr-4 + 0.1 Ni (As Rec'd)	4.70	4.71	7.41	9.87	9.05

Table 8. Oxidation weight gain, integrated area (AMU 4), and dehydride weight gain

Sample	Mass attributable to D_2O cracking	Integrated area (A*s) X 10^{-10}	Weight gain in Ar (mg)
Zr-4 – Ox	0.174	0.274	12.30
Zr-4 + 0.1 Ni – Ox	1.37	15.1	10.88
Zr-4 + 0.2 Ni – Ox	0.346	0.195	13.69
Zr-4 + 0.3 Ni – Ox	0.740	2.20	11.19
Zr-4 + 0.4 Ni – Ox	0.686	1.96	11.46
Zr-4 + 0.1 Ni (As Rec'd)	0	0	12.60
Zr-4 + 0.1 Ni (As Rec'd – N_2 Test)	0	0	0.156

Figure 1. Macrophotograph of the surface modified Zr-4 liners.

Figure 2. Photograph of an EDM sample showing the overall size and support notch after testing.

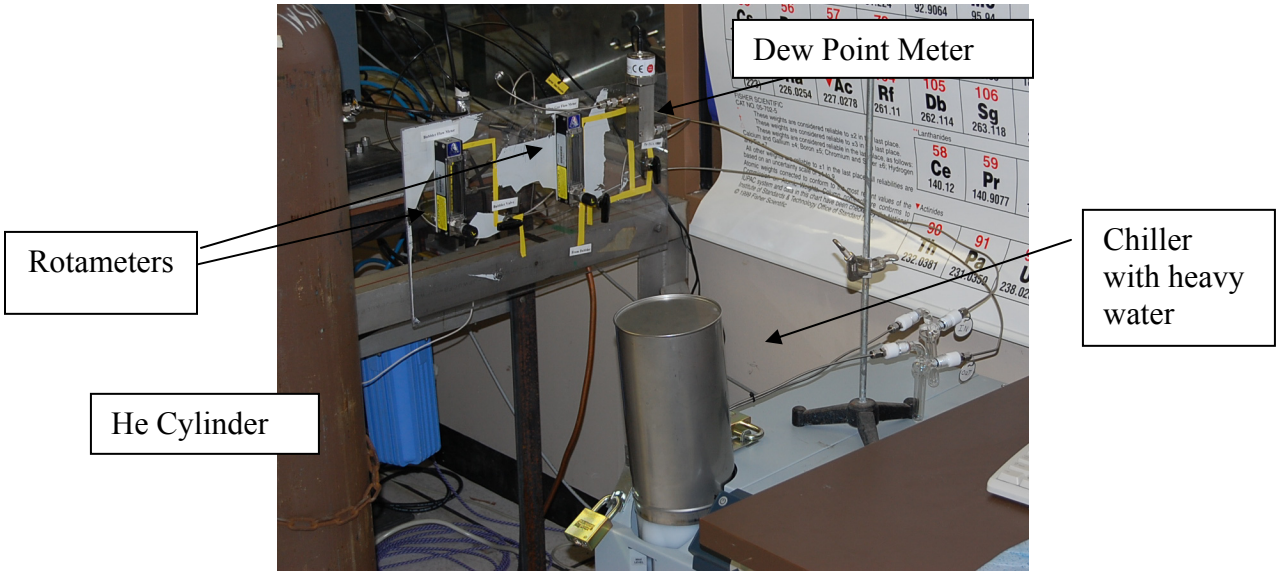

Figure 3. Photograph of the gas delivery system.

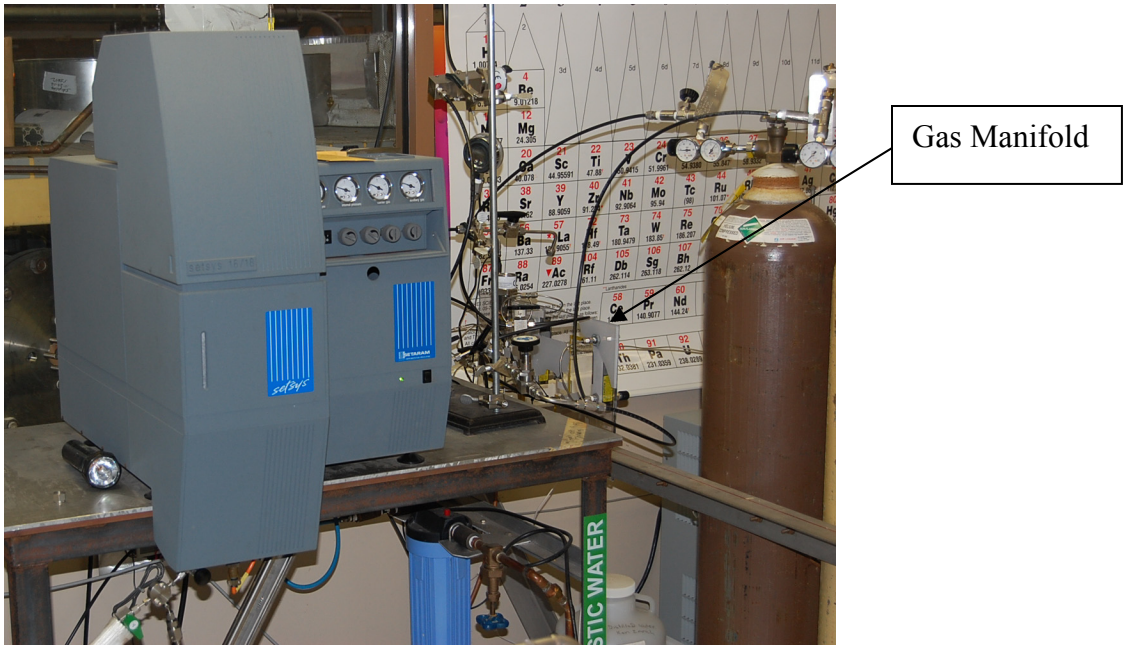

Figure 4. Photograph of the Setaram SetSys TGA.

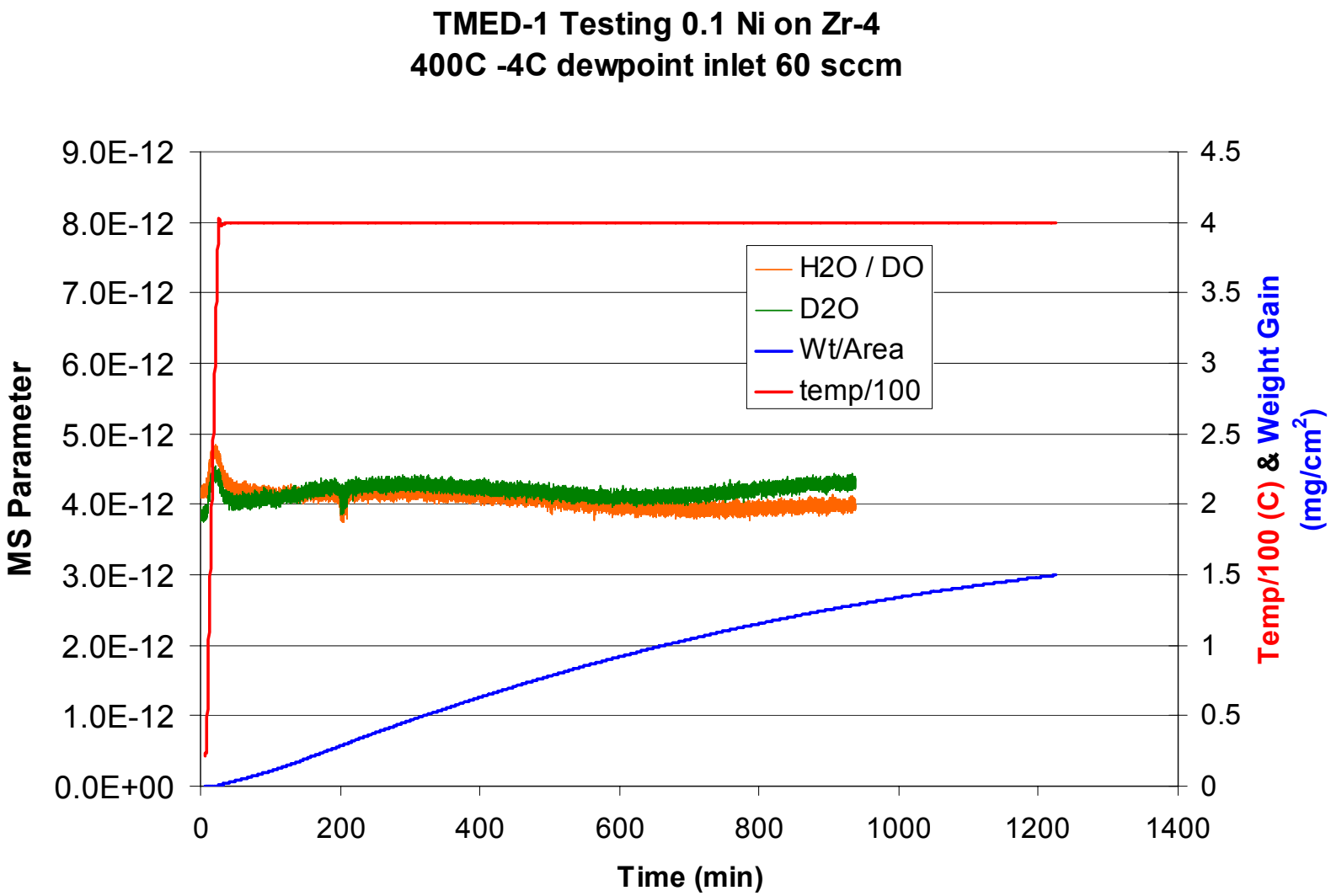

Figure 5. Coupled MS-TGA data for 0.1 mil Ni SM Zr-4 sample.

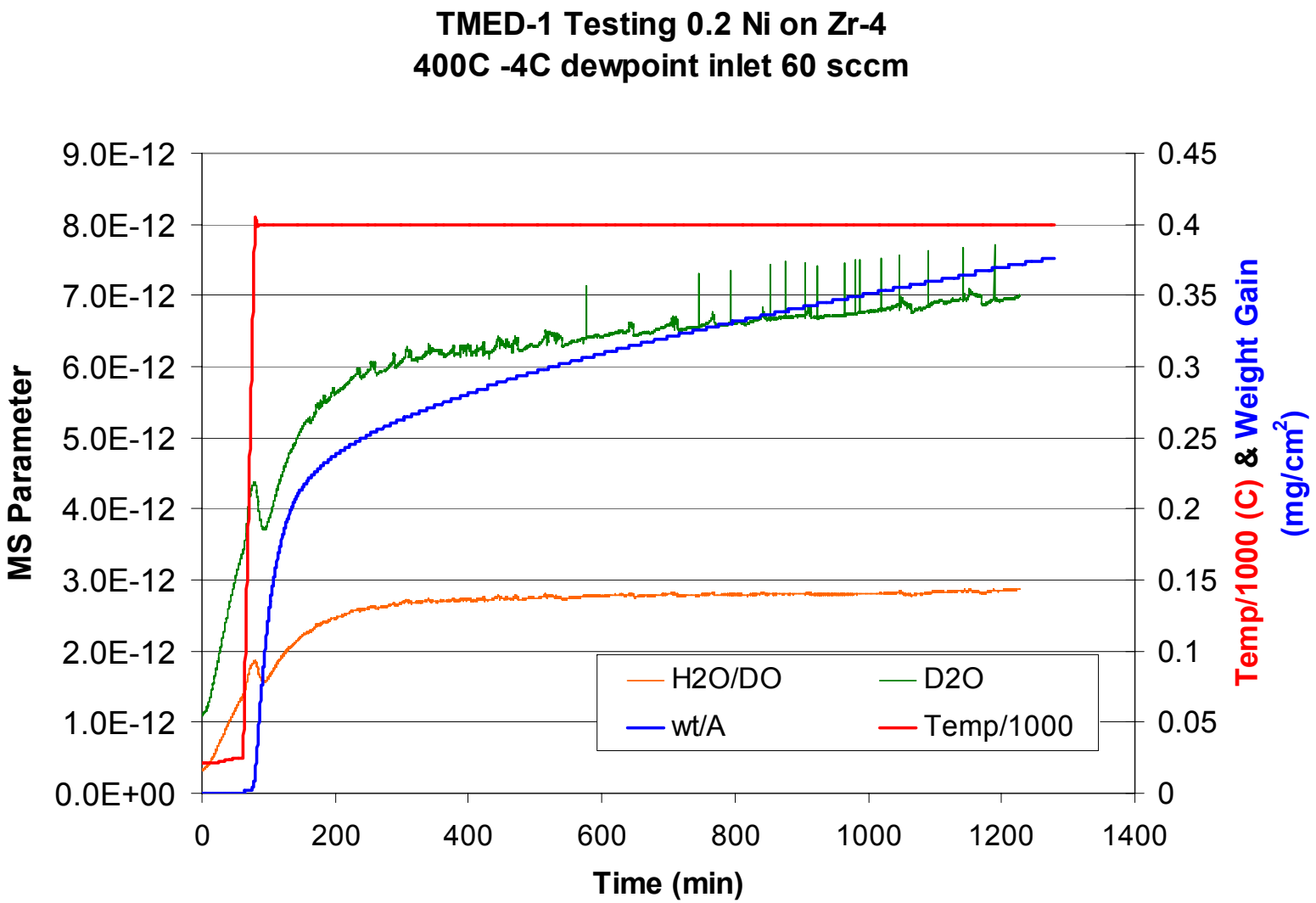

Figure 6. Coupled MS-TGA data for 0.2 mil Ni SM Zr-4 sample.

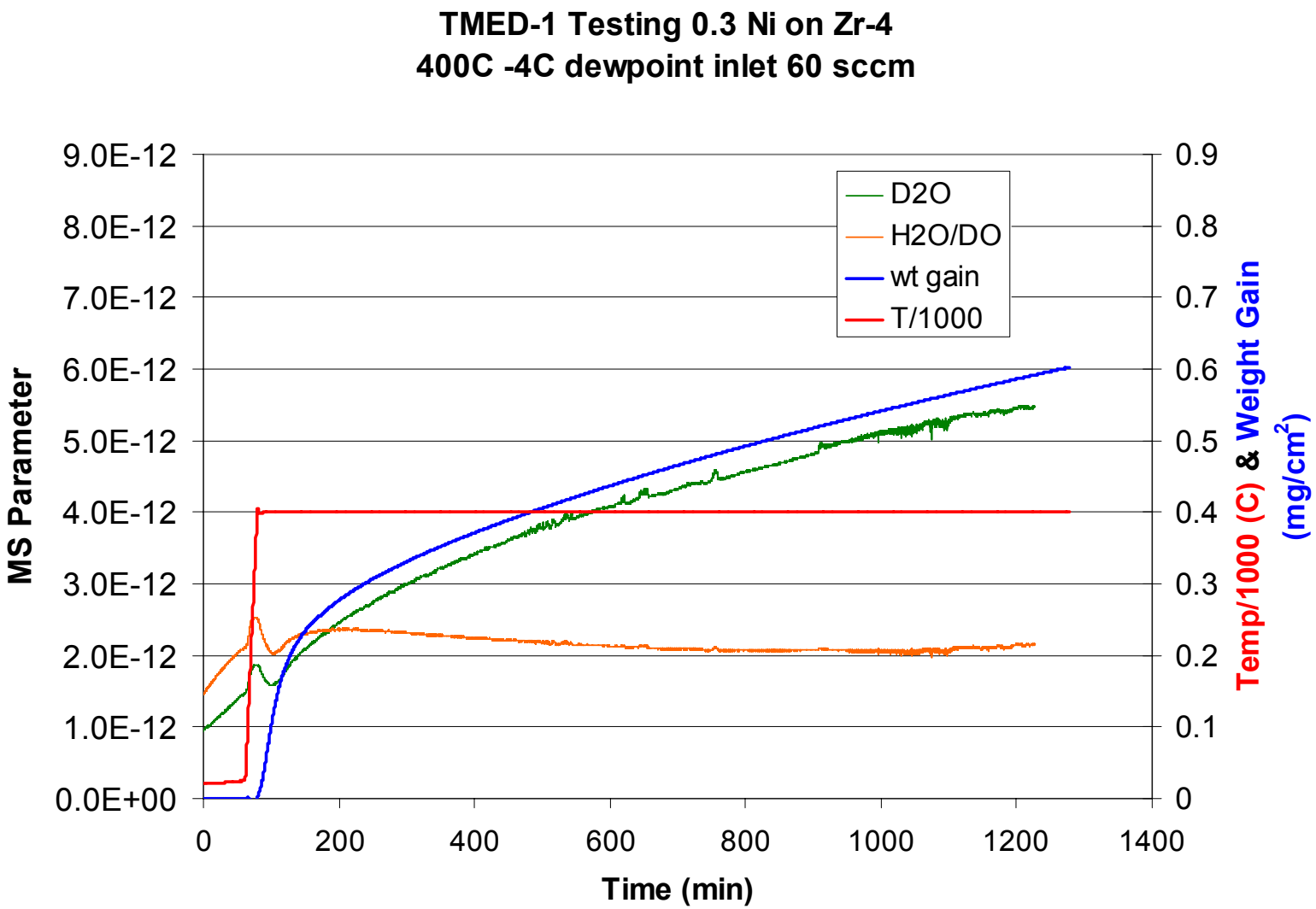

Figure 7. Coupled MS-TGA data for 0.3 mil Ni SM Zr-4 sample.

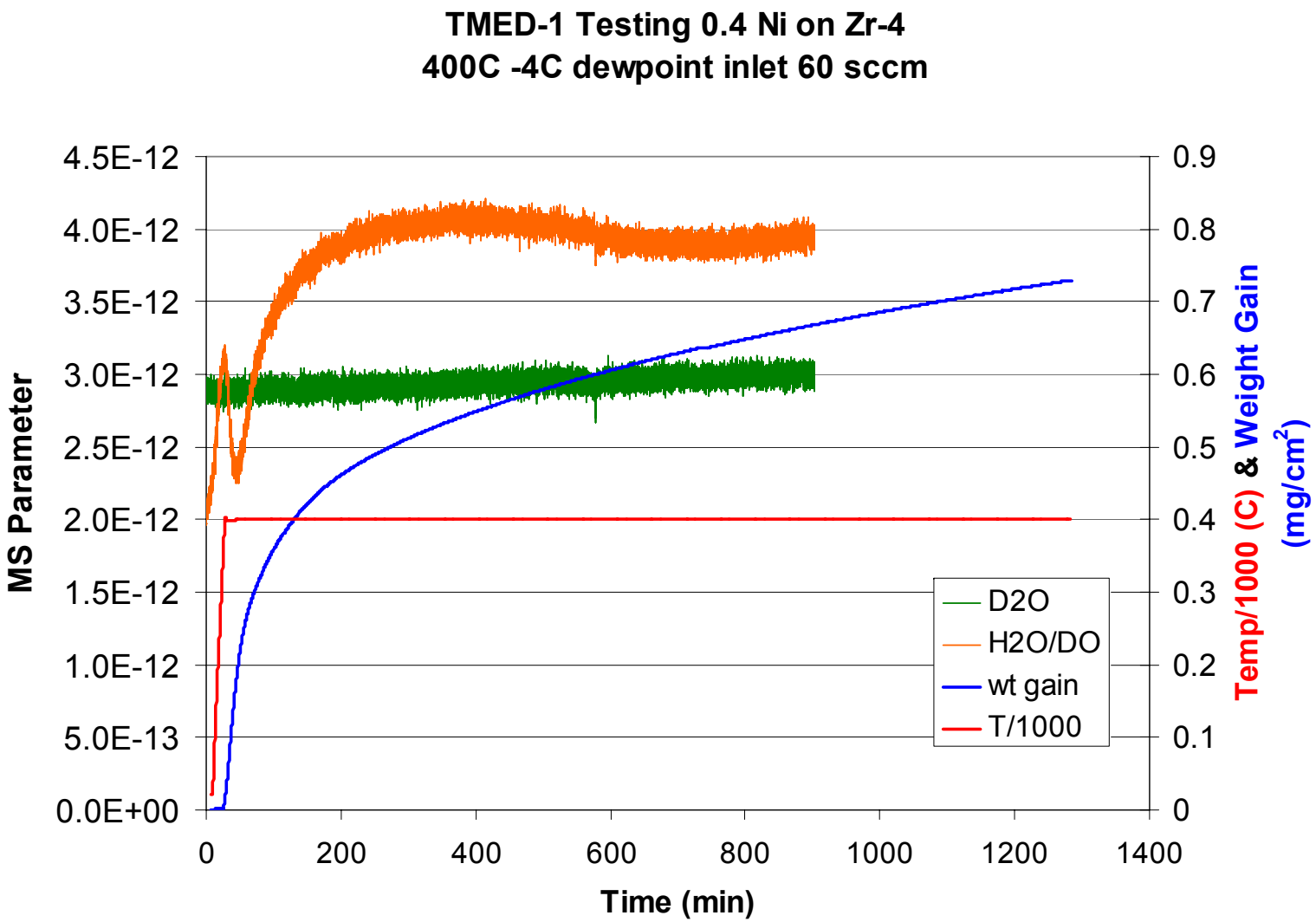

Figure 8. Coupled MS-TGA data for 0.4 mil Ni SM Zr-4 sample.

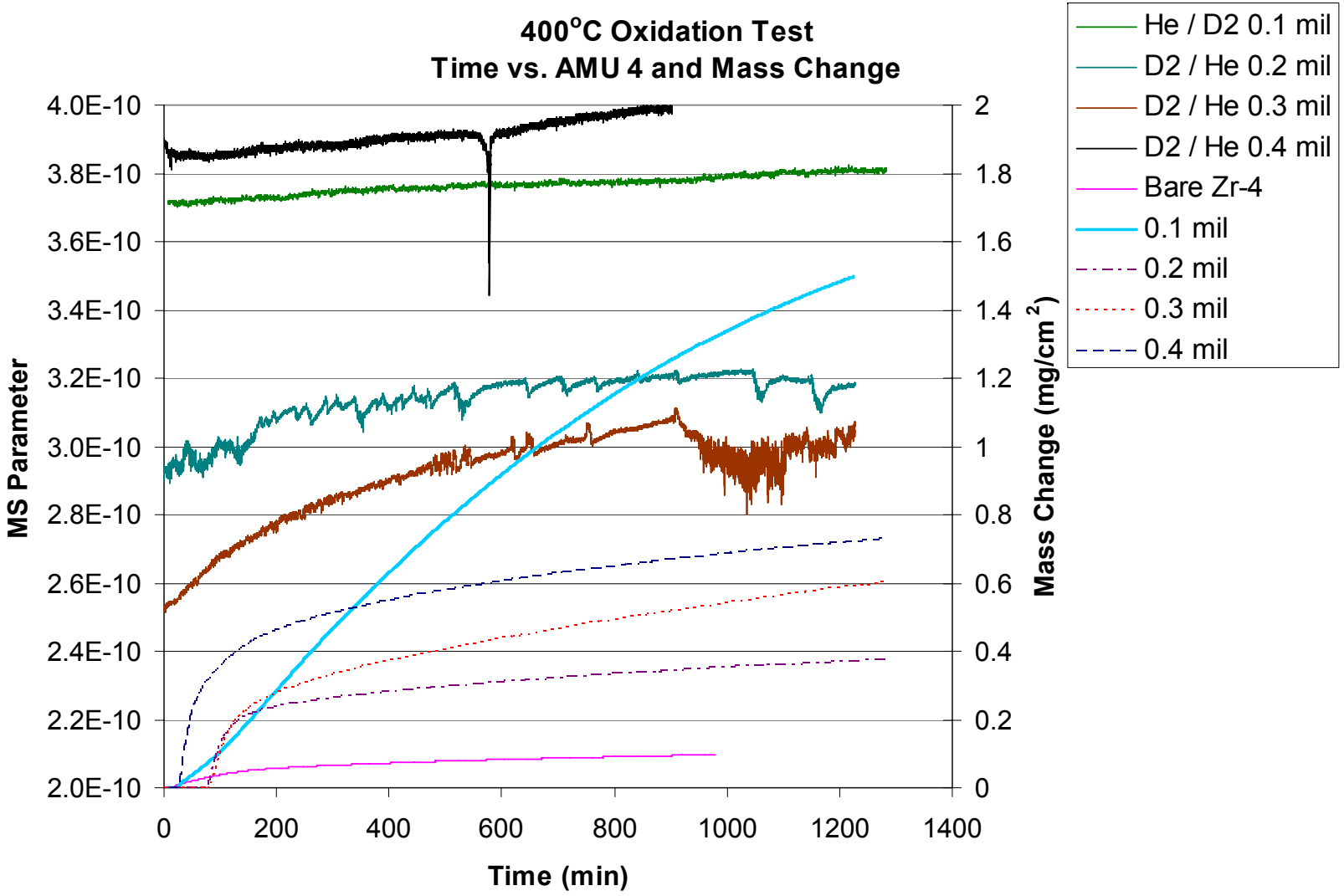

Figure 9. TGA data from as-received and nickel plated SM Zr-4 tested at 400°C.

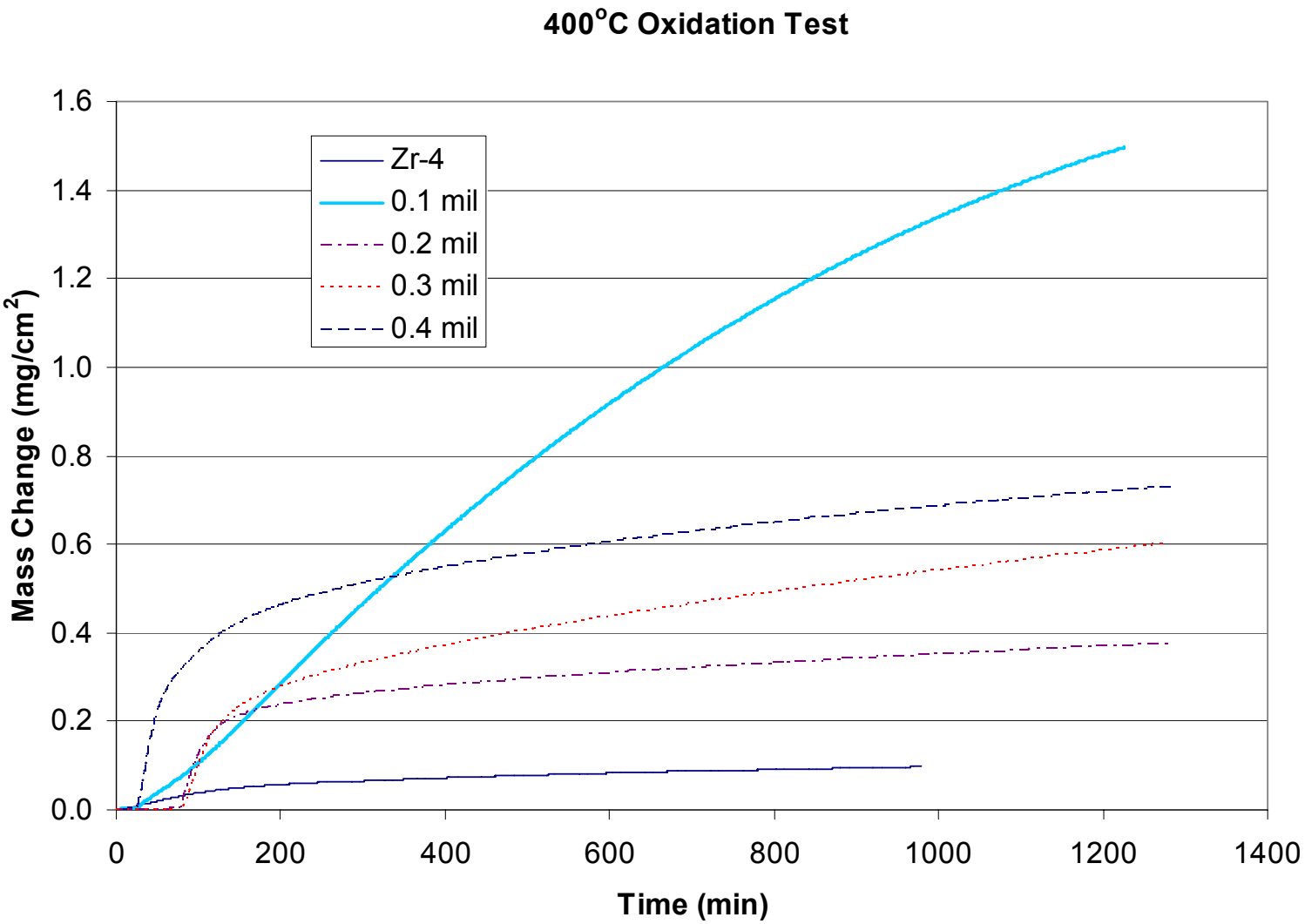

Figure 10. 400°C oxidation test results for as-received and SM Zr-4

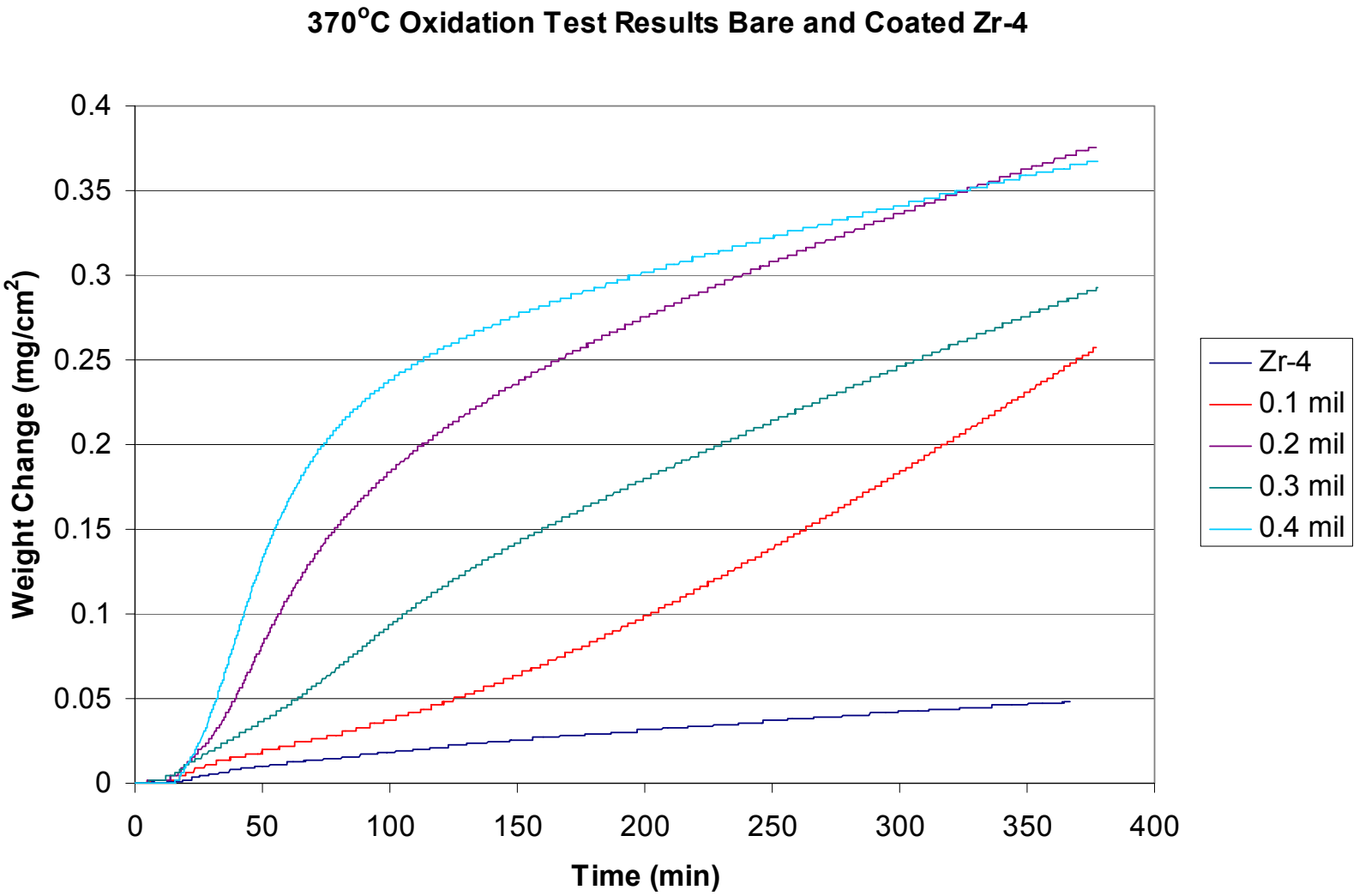

Figure 11. Oxidation data from as-received and SM Zr-4 samples tested at 370°C.

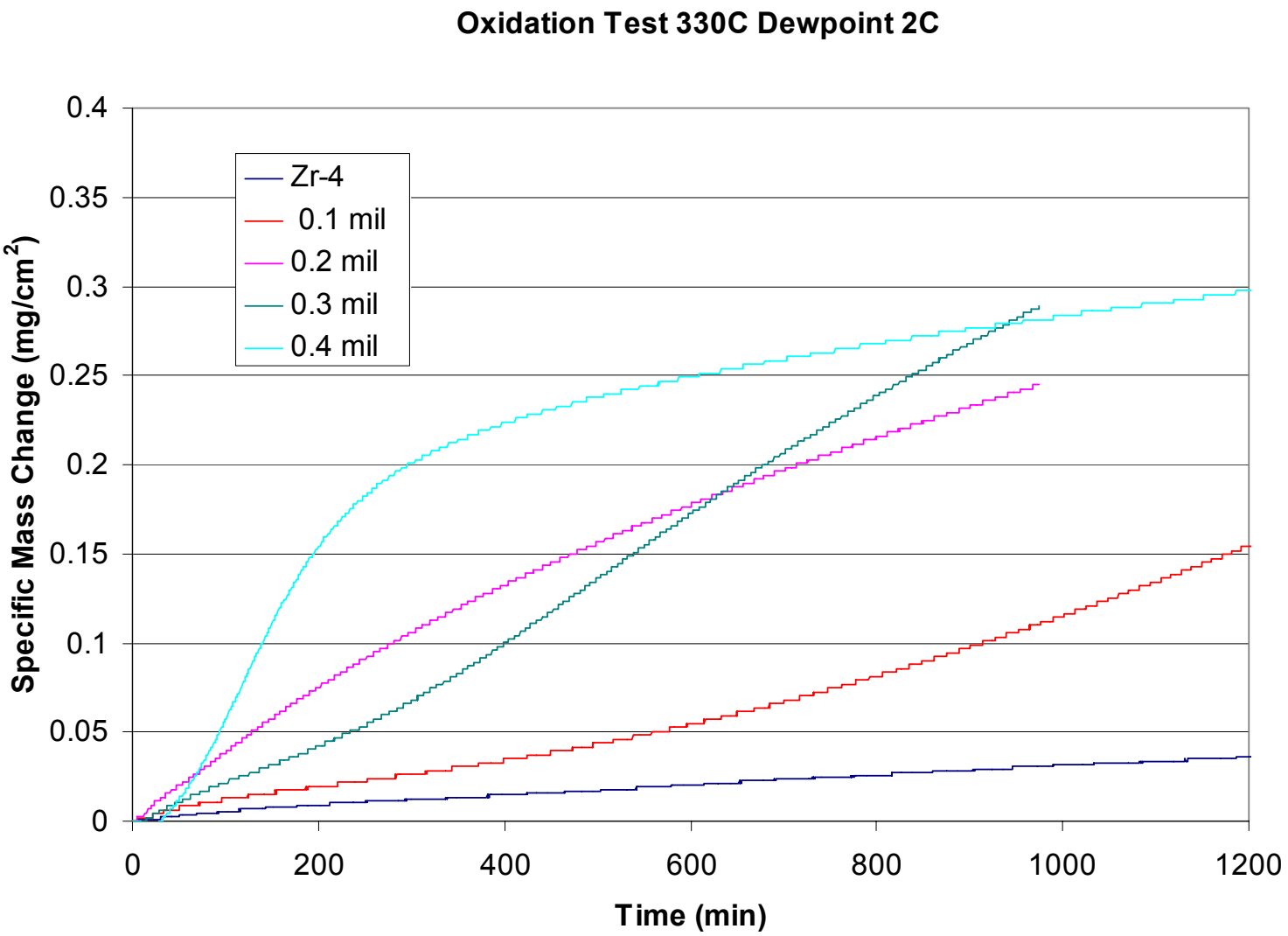

Figure 12. Oxidation data from as-received and SM Zr-4 samples tested at 330°C.

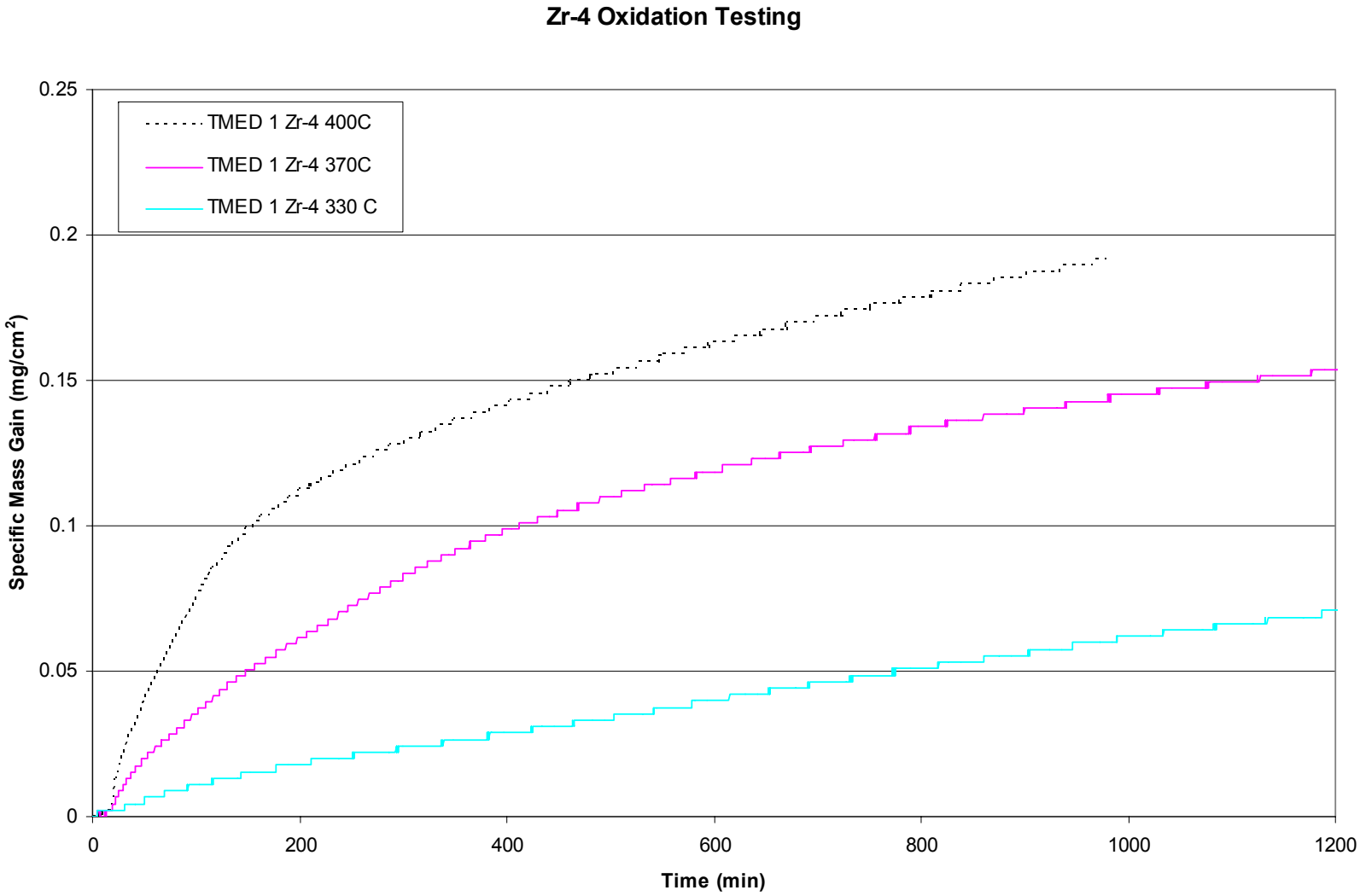

Figure 13. As received Zr-4 oxidation data vs. temperature

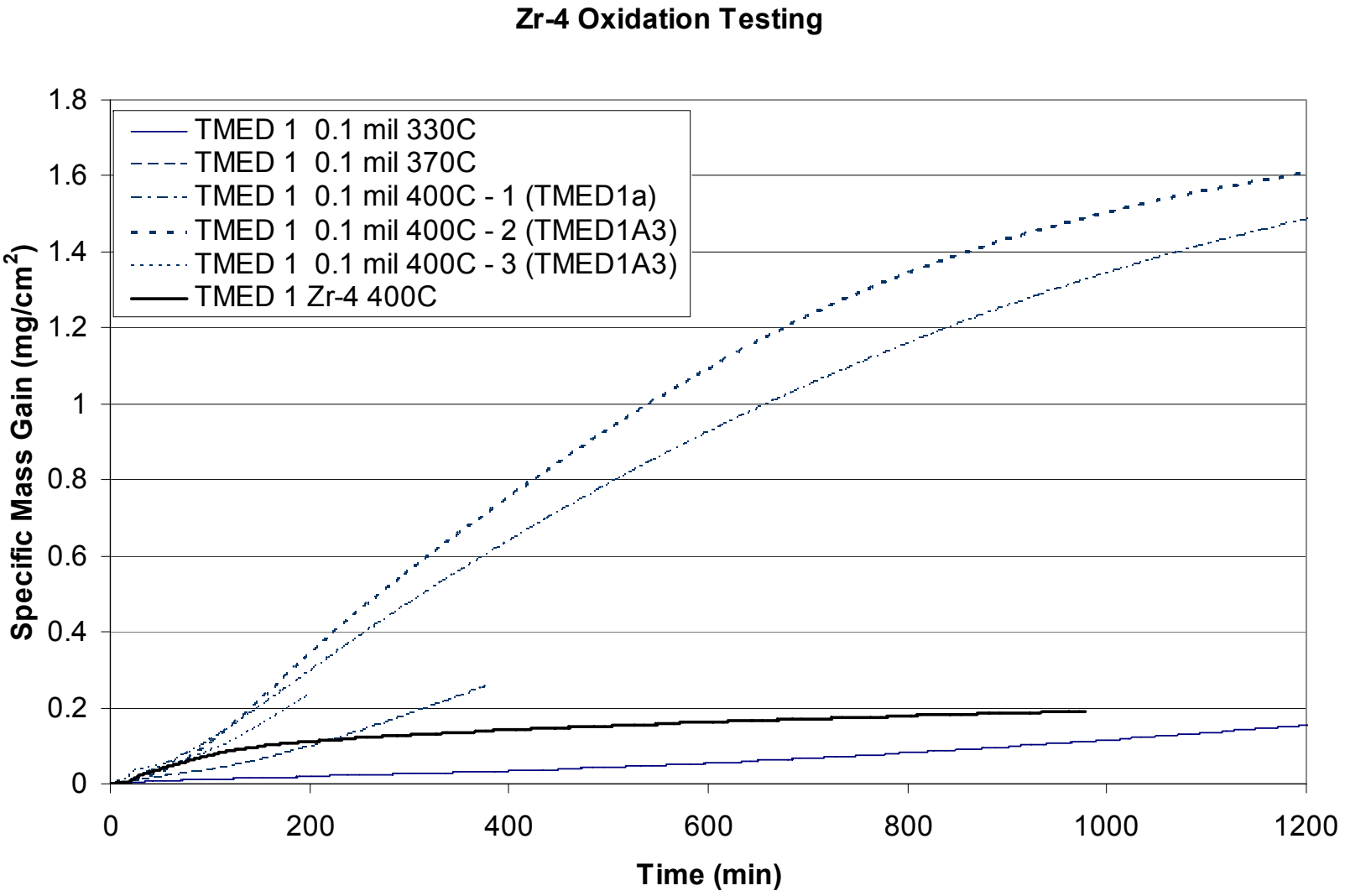

Figure 14. 0.1 mil Ni SM Zr-4 oxidation data vs. temperature

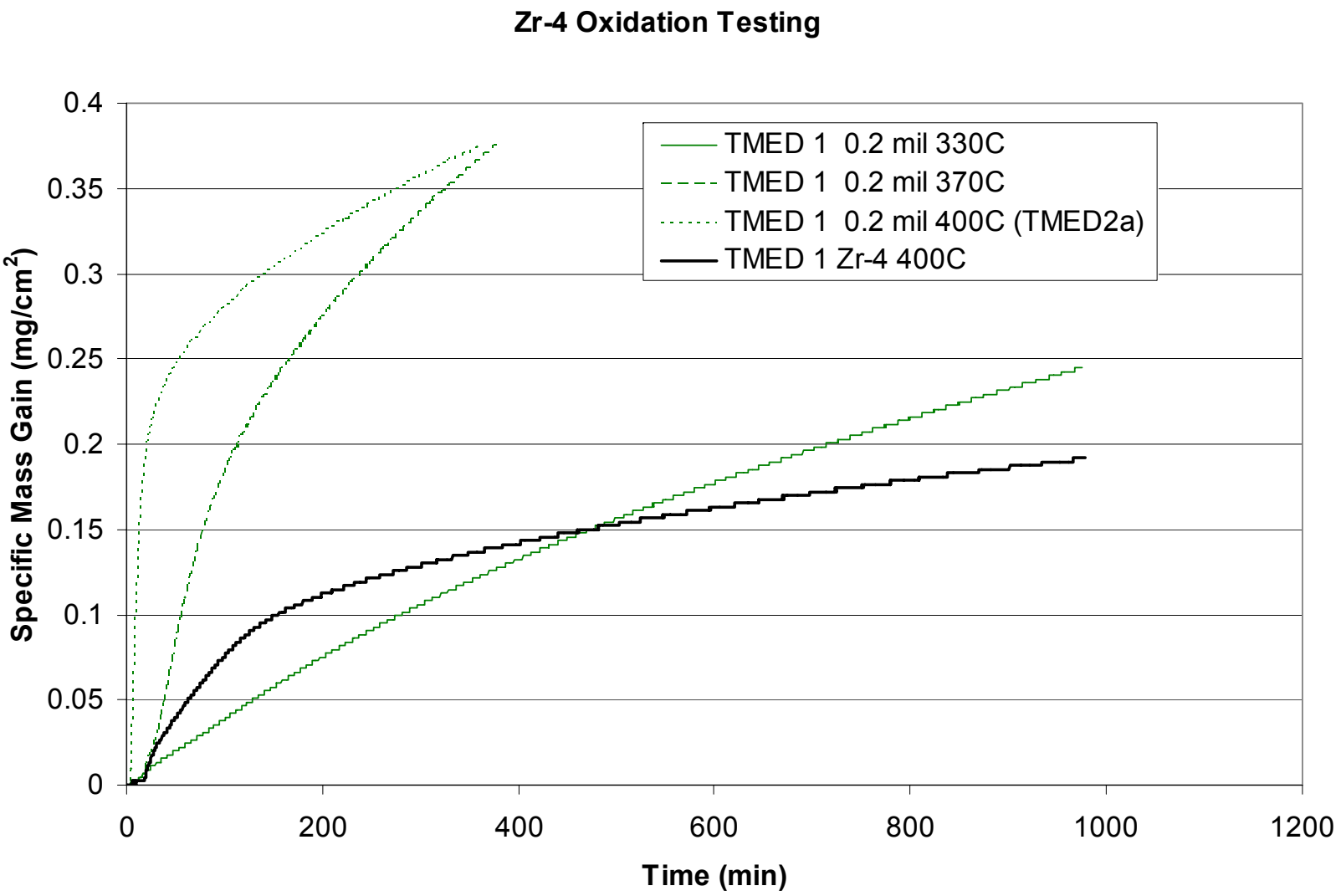

Figure 15. 0.2 mil SM Zr-4 oxidation data vs. temperature

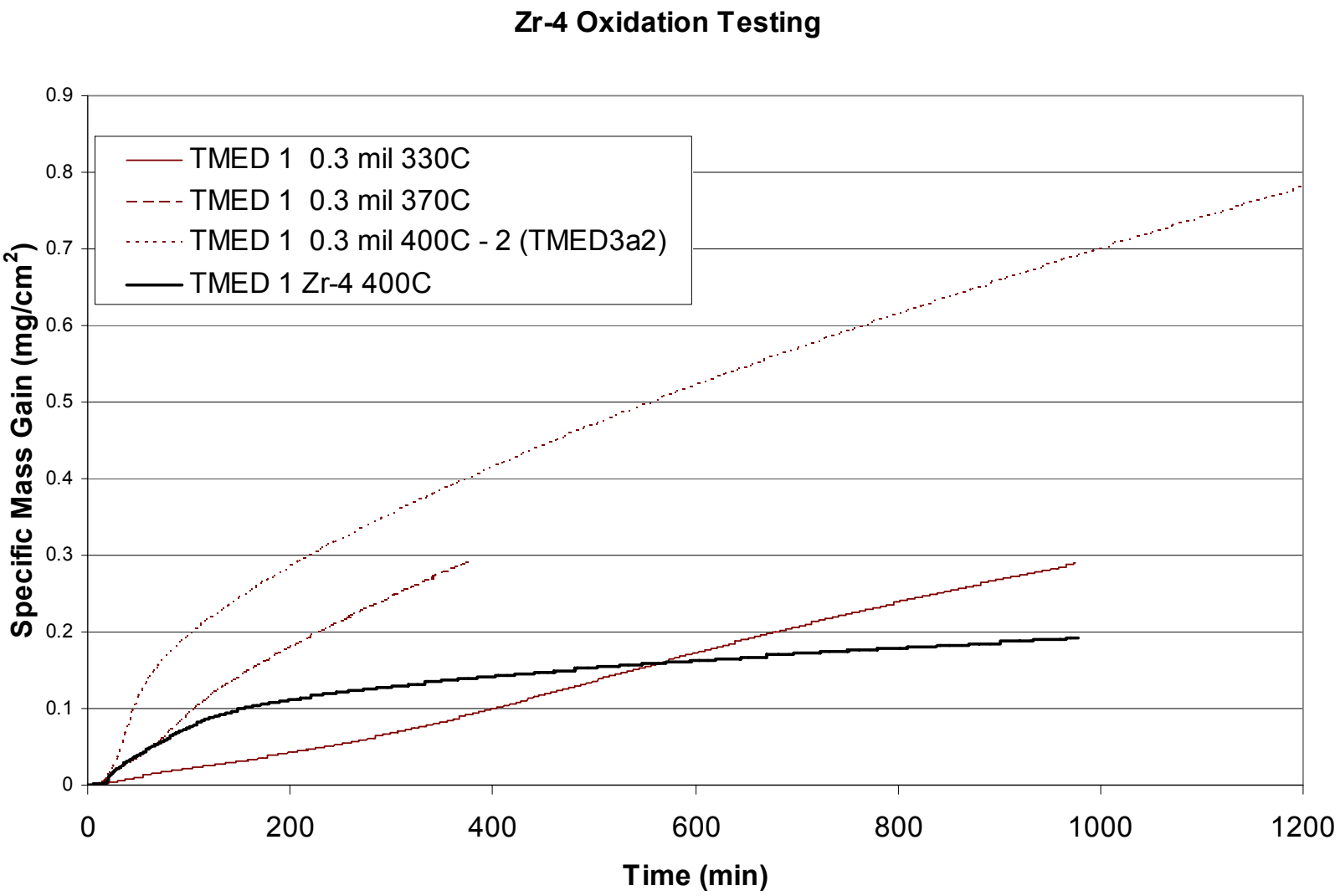

Figure 16. 0.3 mil Ni SM Zr-4 oxidation data vs. temperature

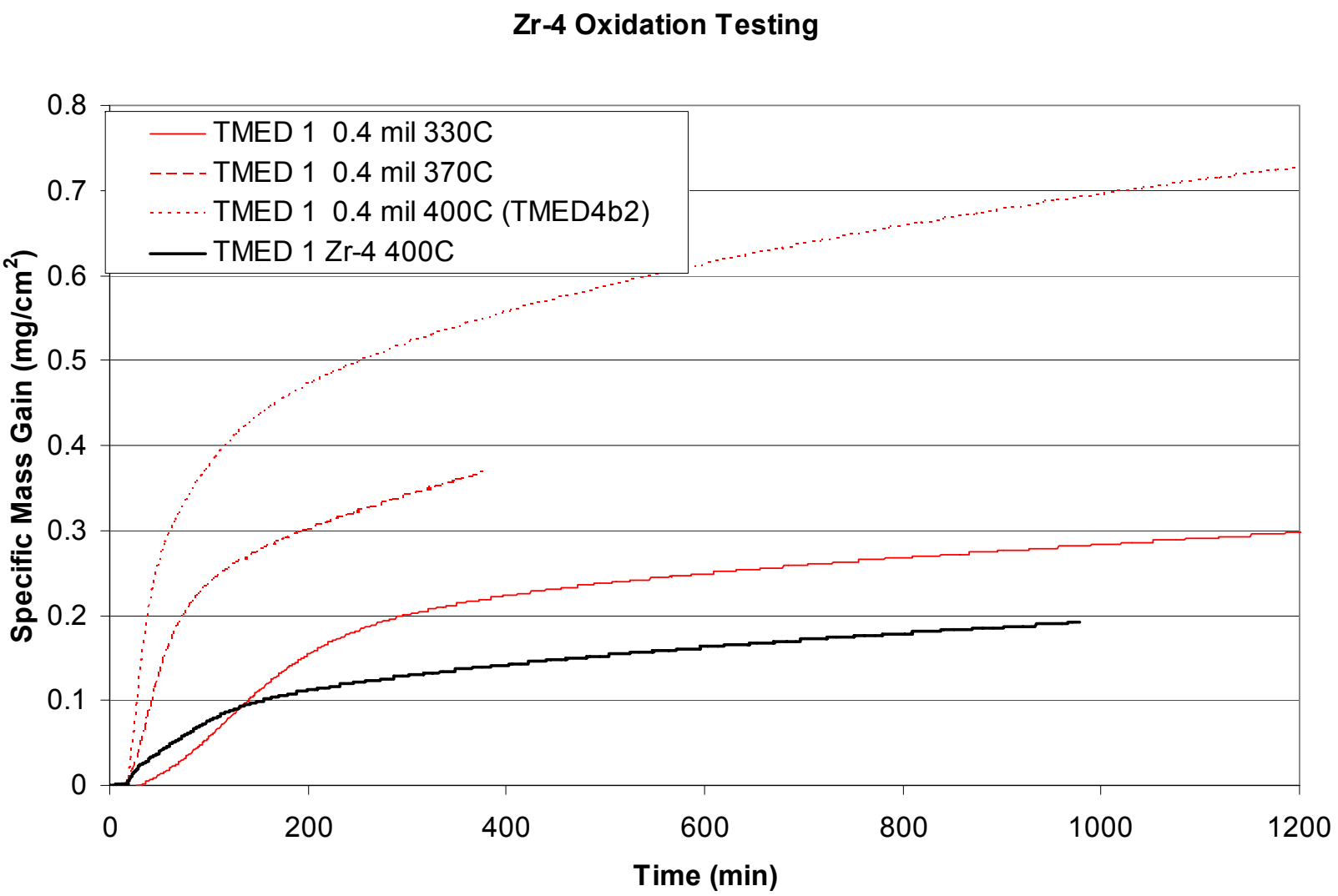

Figure 17. 0.4 mil Ni SM Sr-4 oxidation data vs. temperature

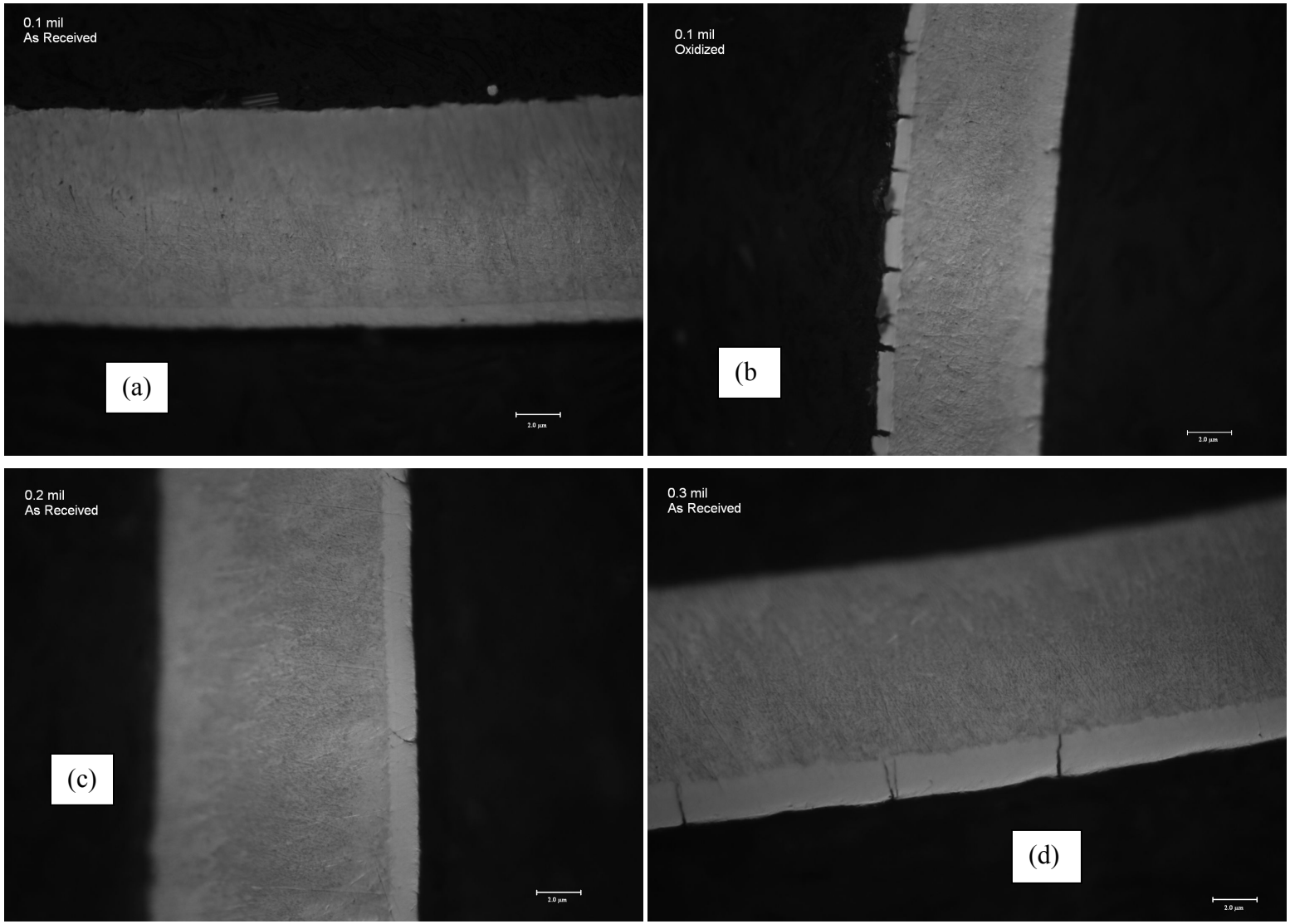

Figure 18. Metallographic cross sections of the (a) as received 0.1 mil SM Zr-4 (b) oxidized 0.1 mil SM Zr-4 (c) as received 0.2 mil SM Z4-4 and (d) as received 0.3 mil SM Zr-4.

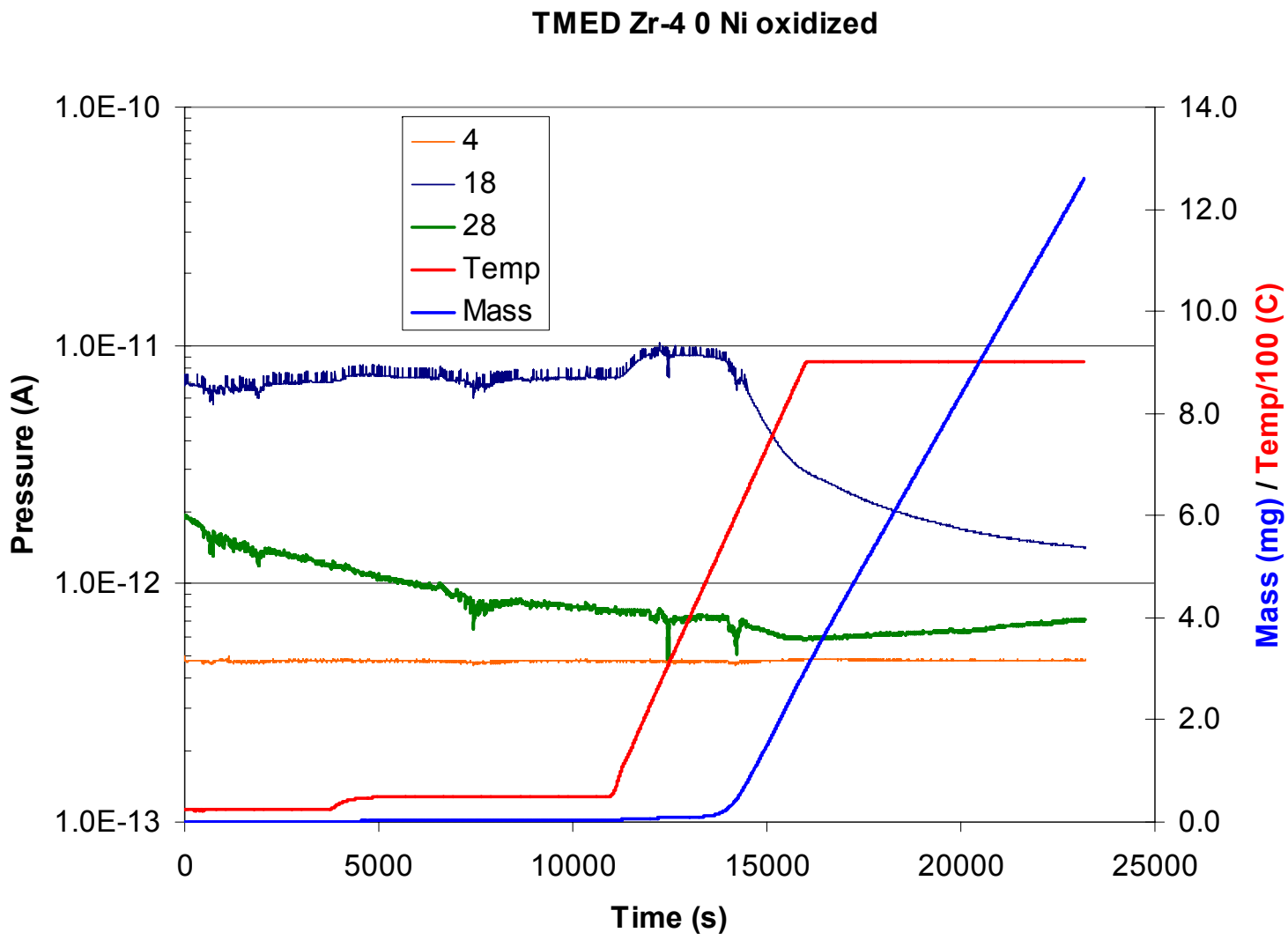

Figure 19. As-received Zr-4 after deuterium oxide exposure at 400°C / 20 hours and subsequent thermal exposure to 900°C at a heating rate at 10°C/min.

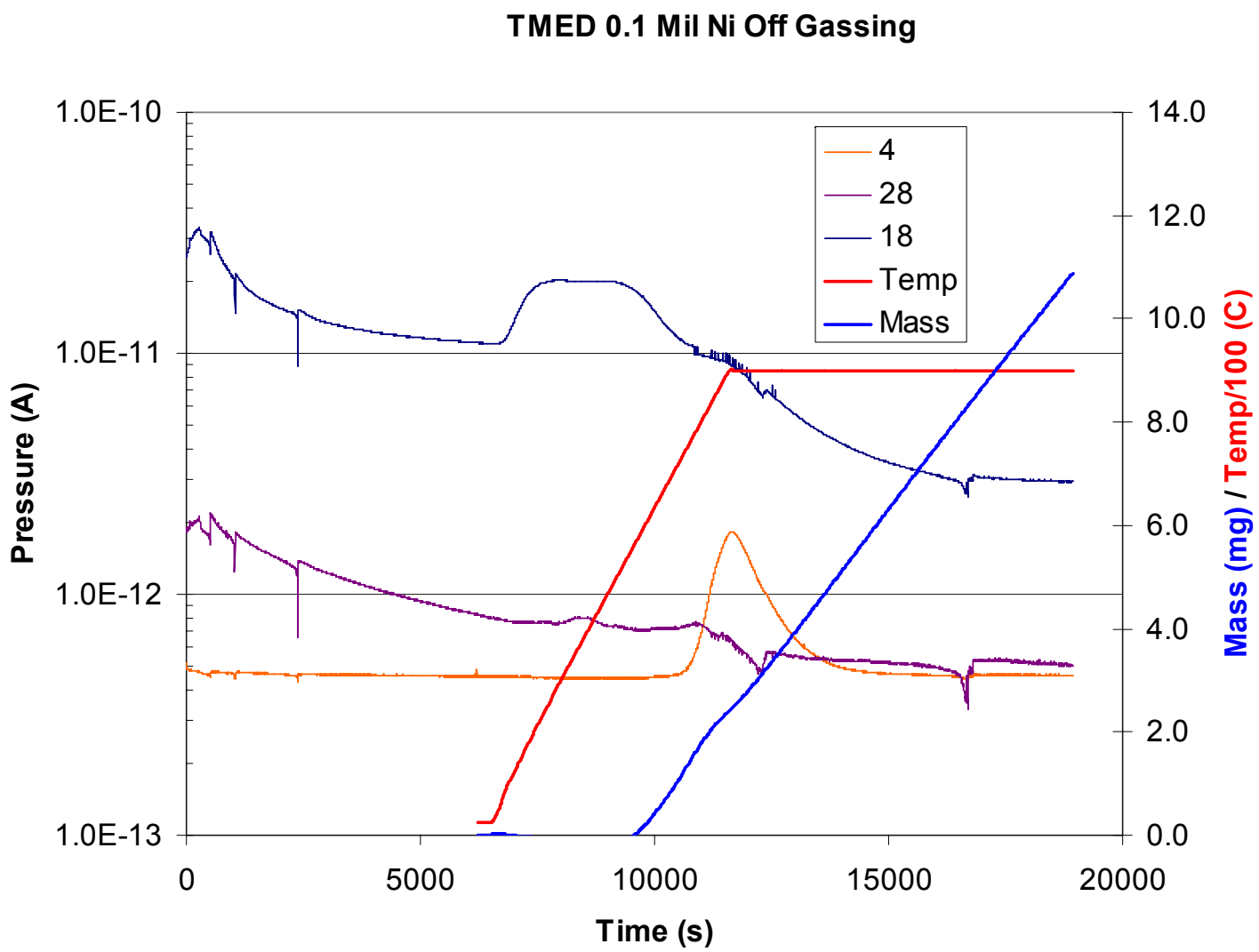

Figure 20. 0.1 mil Ni plated SM Zr-4 after deuterium oxide exposure at 400°C / 20 hours and subsequent thermal exposure to 900°C at a heating rate at 10°C/min. – Note AMU 4 peak.

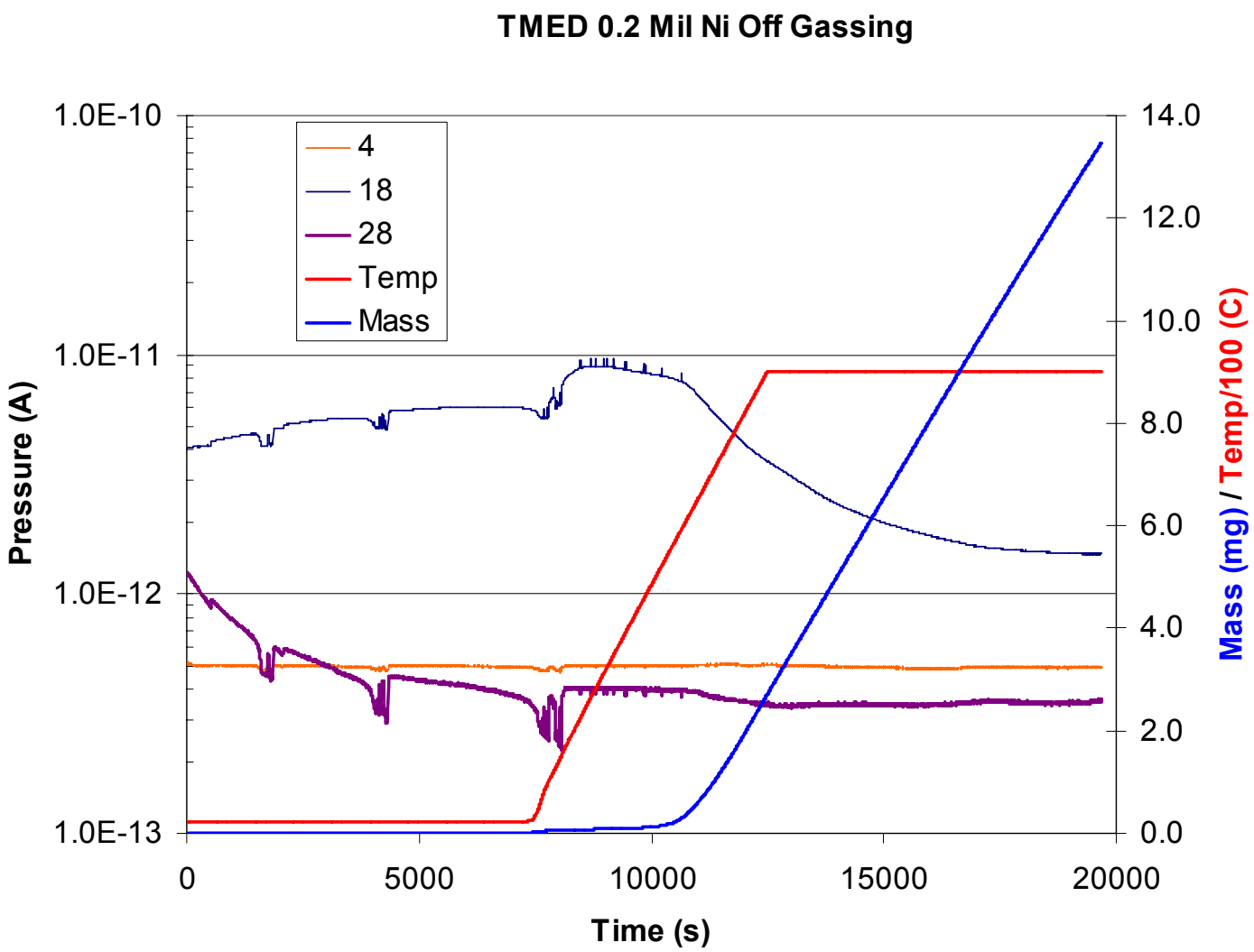

Figure 21. 0.2 mil Ni plated SM Zr-4 after deuterium oxide exposure at 400°C / 20 hours and subsequent thermal exposure to 900°C at a heating rate at 10°C/min. Note—no real AMU 4 peak.

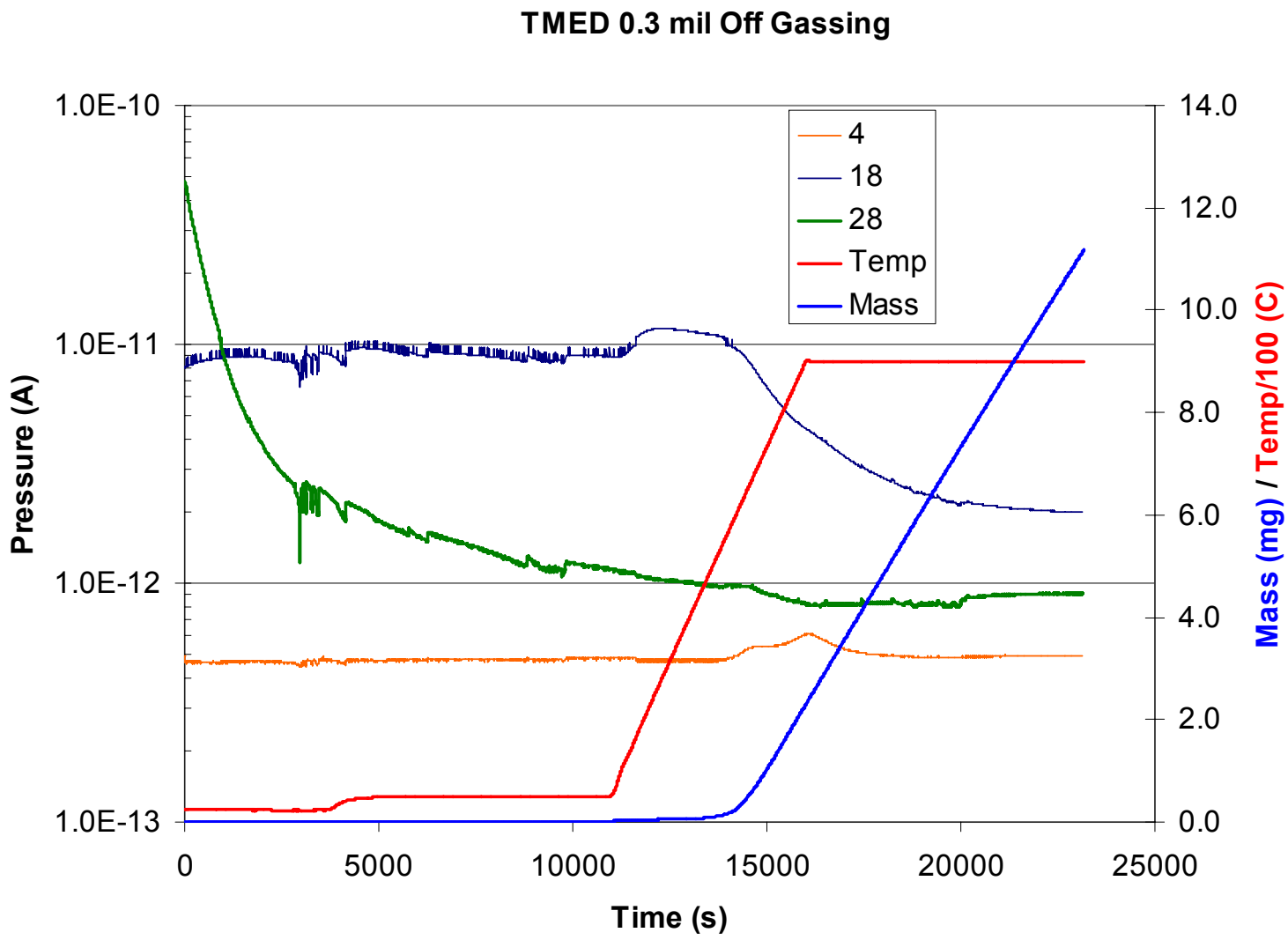

Figure 22. 0.3 mil Ni plated SM Zr-4 after deuterium oxide exposure at 400°C / 20 hours and subsequent thermal exposure to 900°C at a heating rate at 10°C/min. Note—Obvious AMU 4 peak.

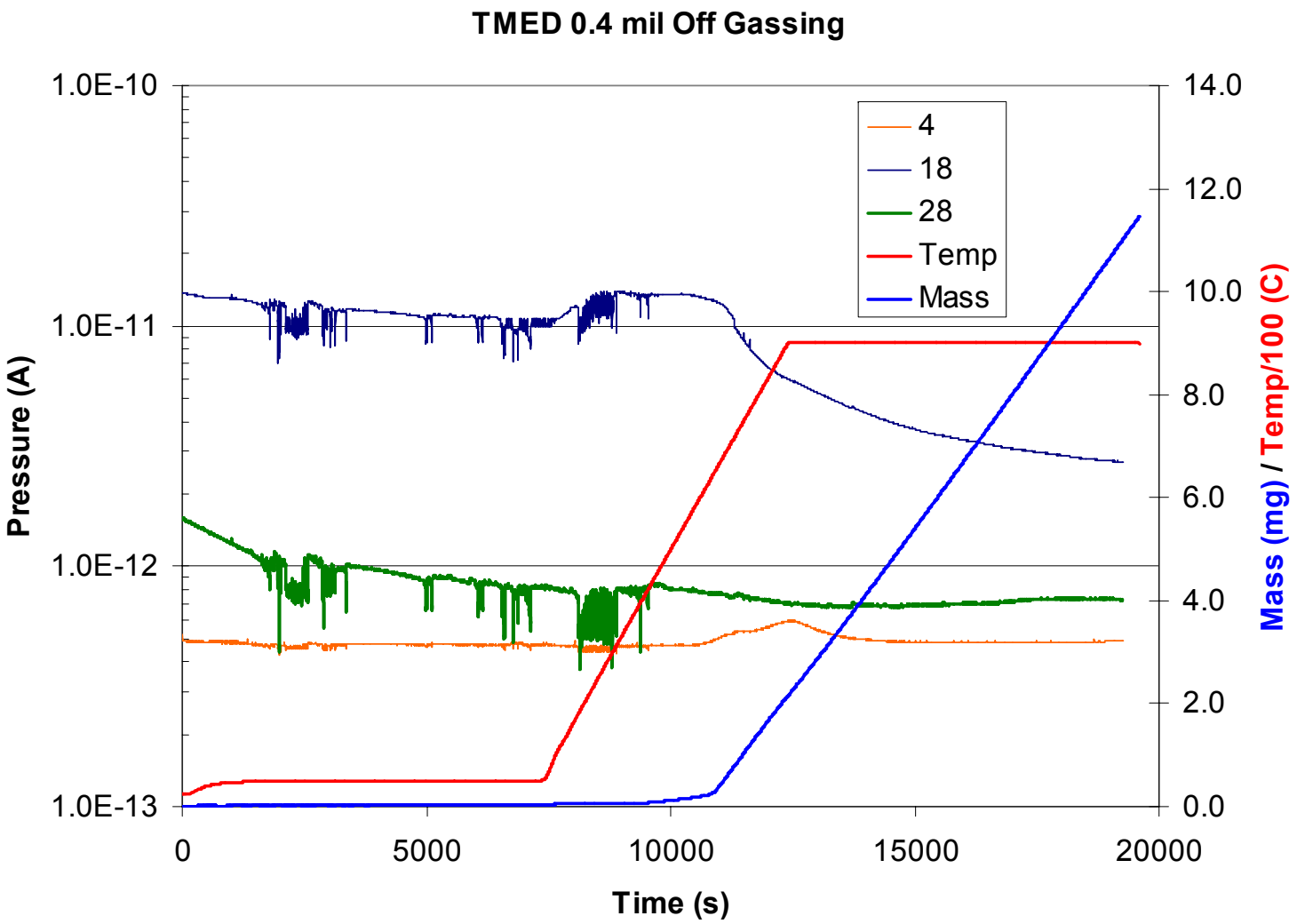

Figure 23. 0.4 mil Ni plated SM Zr-4 after deuterium oxide exposure at 400°C / 20 hours and subsequent thermal exposure to 900°C at a heating rate at 10°C/min.

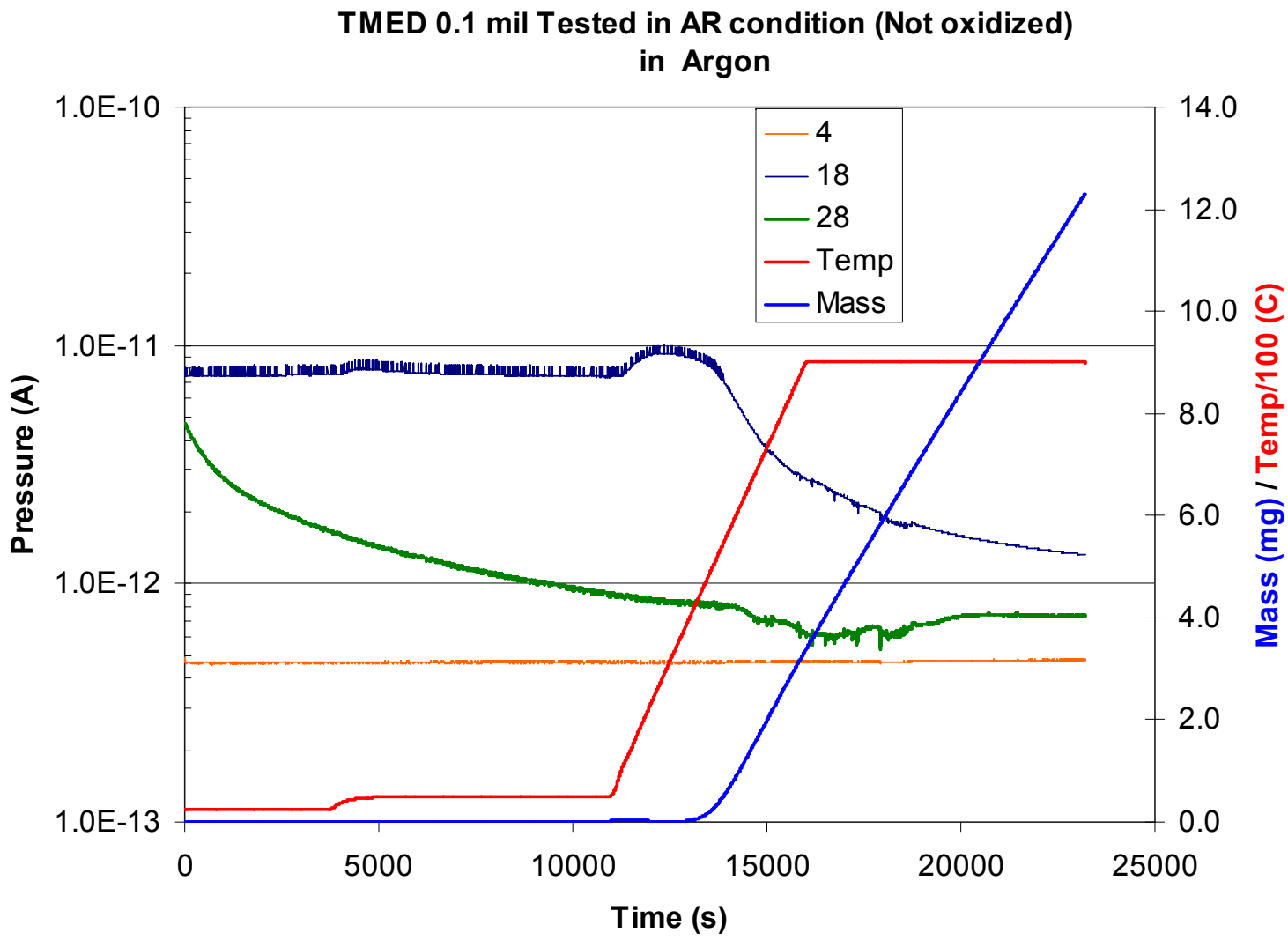

Figure 24. 0.1 mil Ni plated SM Zr-4 in as received condition subjected to thermal exposure of 900°C at a heating rate at 10°C/min--Argon.

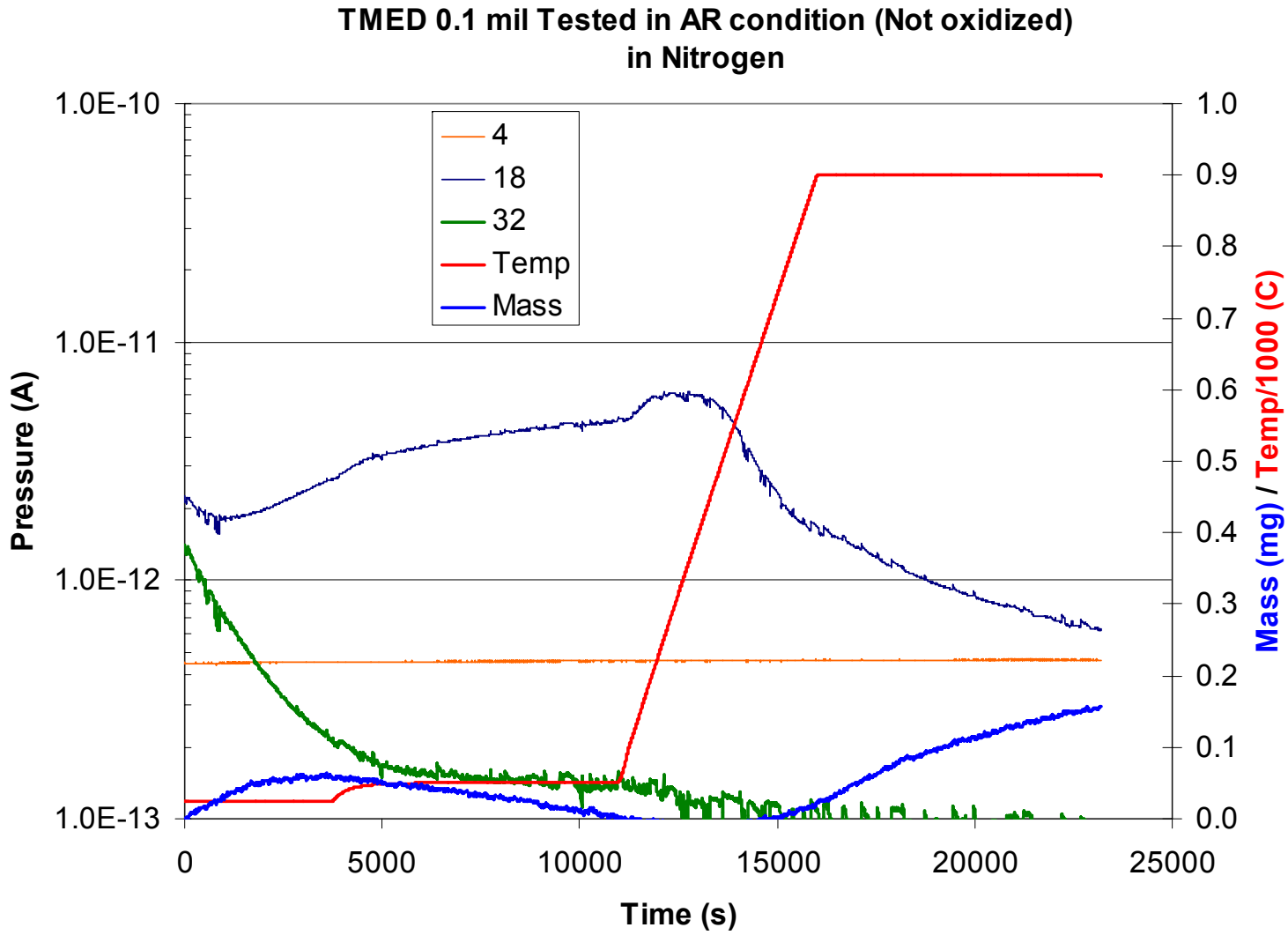

Figure 25. 0.1 mil Ni plated SM Zr-4 in as received condition subjected to thermal exposure of 900°C at a heating rate at 10°C/min--Nitrogen. – Note change of scale.

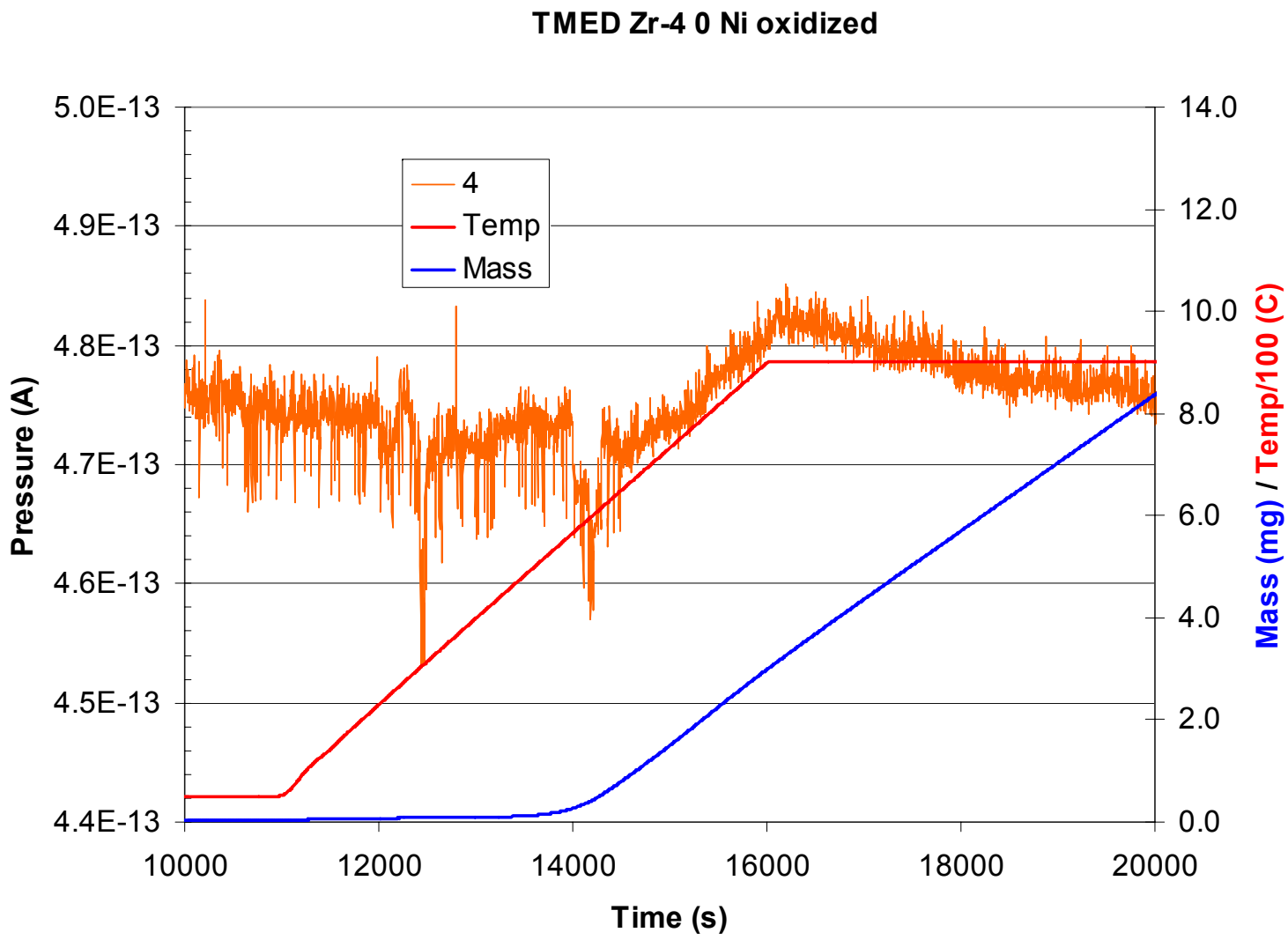

Figure 26. Thermogravimetric and Mass Spectroscopy data showing peak height for AMU 4 for as-received Zr-4 oxidized sample (see Fig. 19).

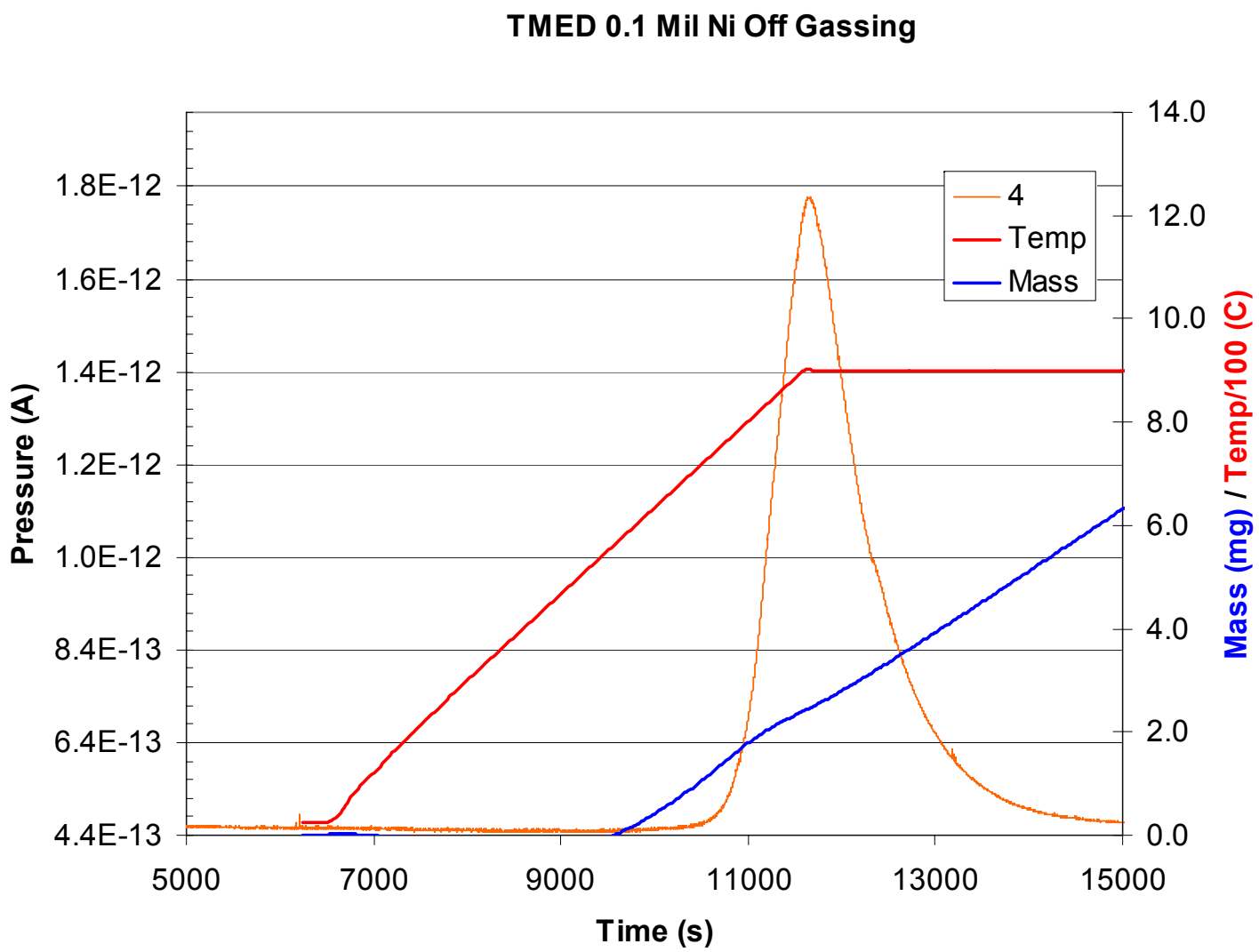

Figure 27. Thermogravimetric and Mass Spectroscopy data showing peak height for AMU 4 for 0.1 mil Ni SM Zr-4 oxidized sample (see Fig. 20).

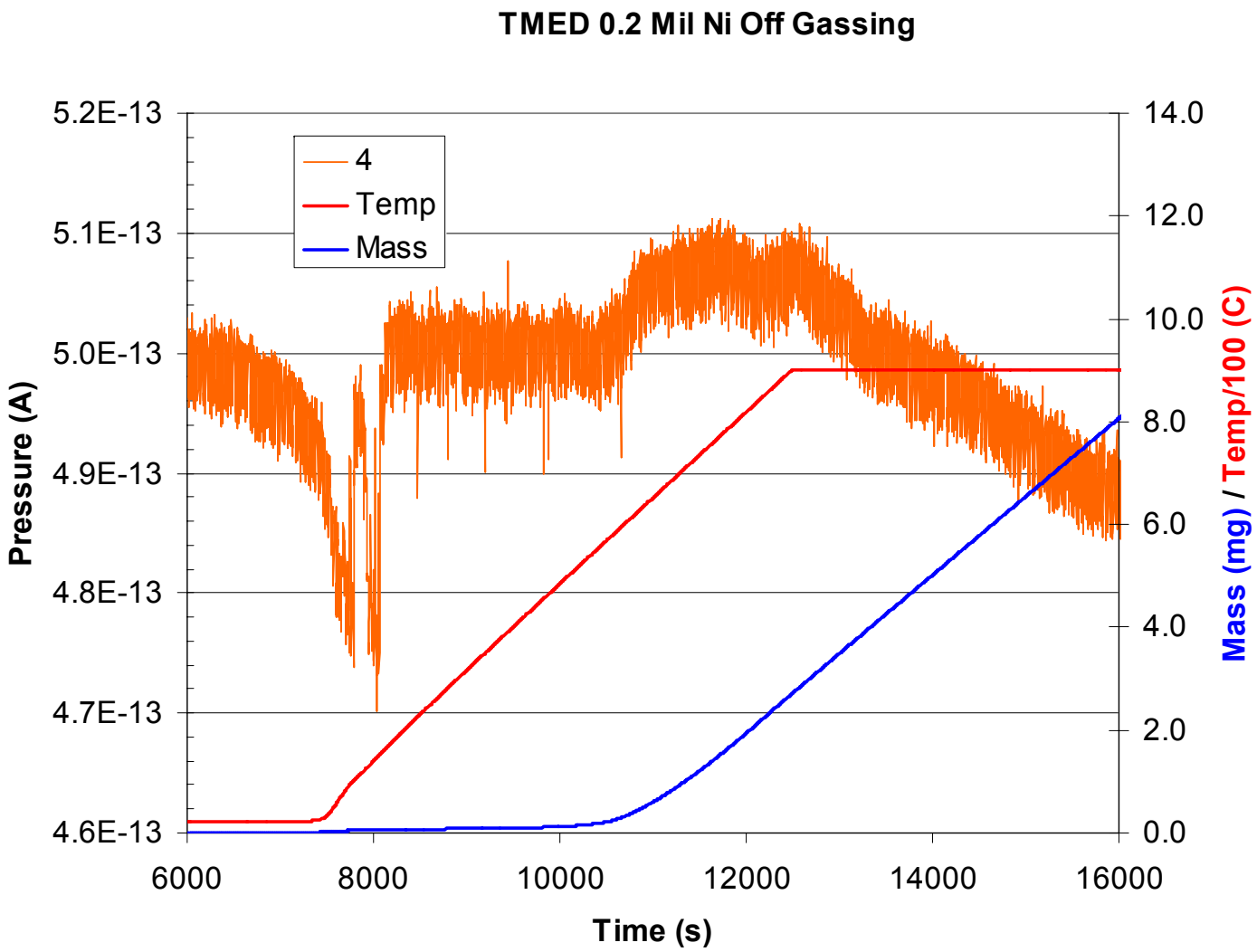

Figure 28. Thermogravimetric and Mass Spectroscopy data showing peak height for AMU 4 for 0.2 mil Ni SM Zr-4 oxidized sample (see Fig. 21).

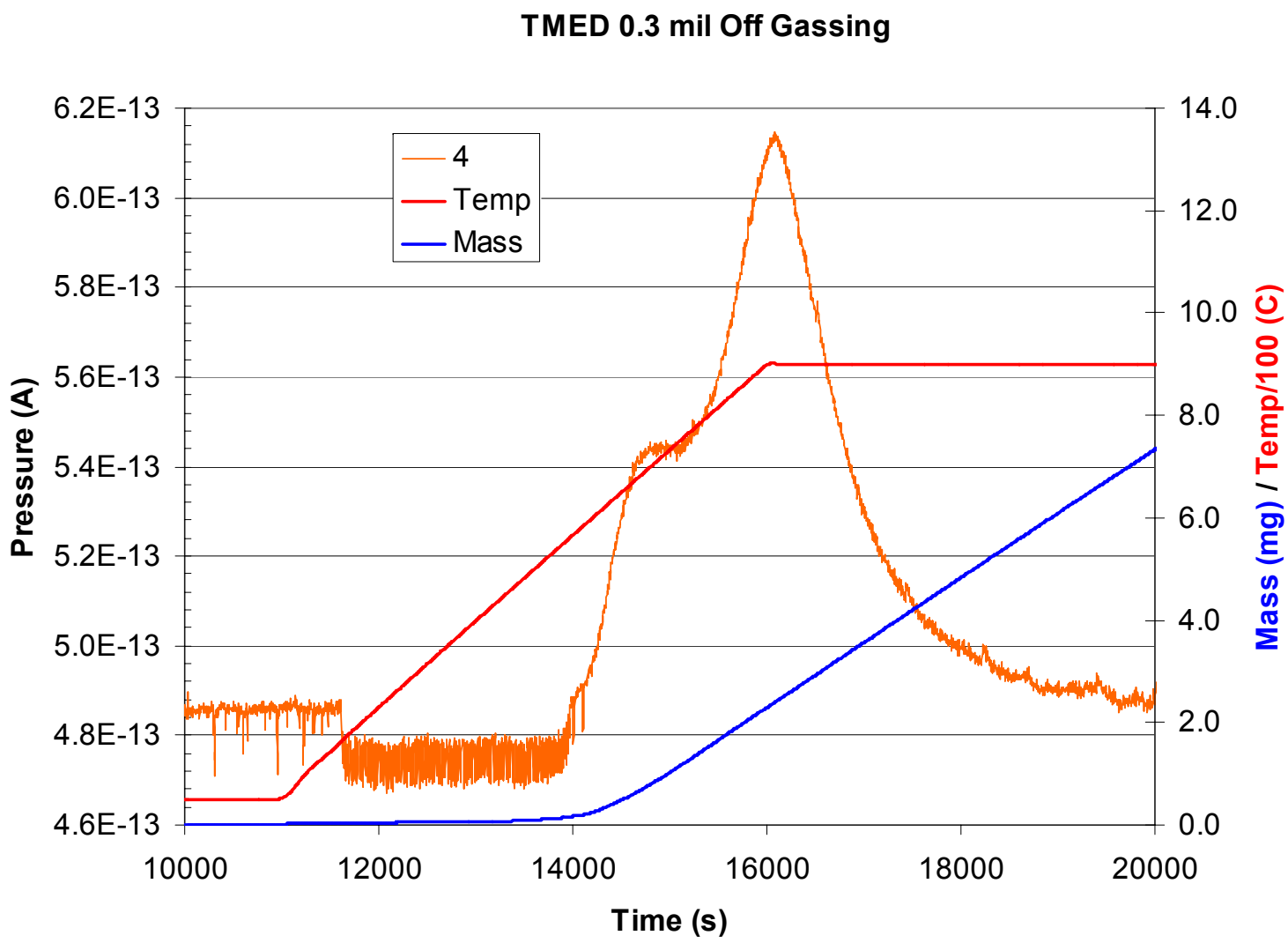

Figure 29. Thermogravimetric and Mass Spectroscopy data showing peak height for AMU 4 for 0.3 mil Ni SM Zr-4 oxidized sample (see Fig. 22).

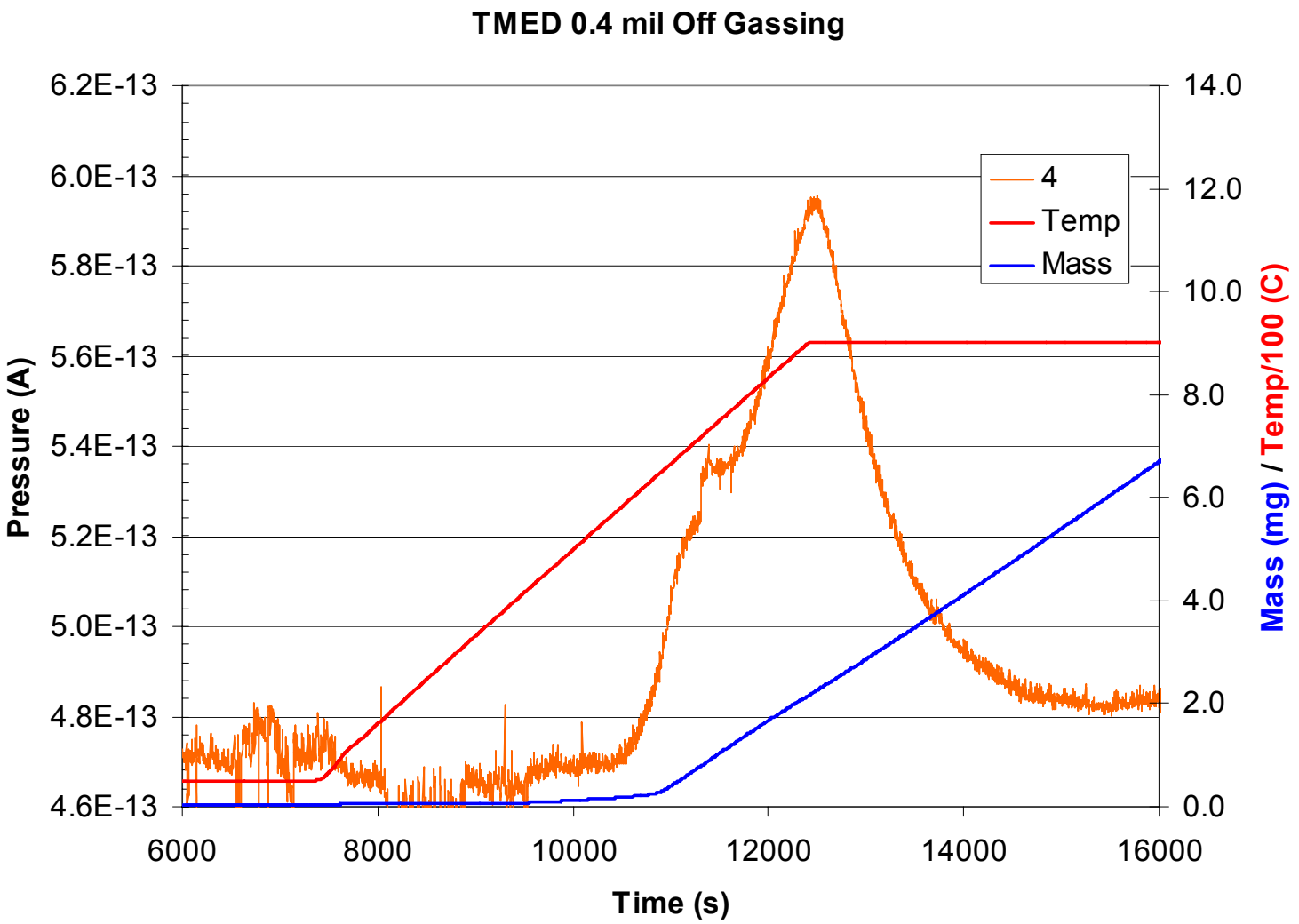

Figure 30. Thermogravimetric and Mass Spectroscopy data showing peak height for AMU 4 for 0.4 mil Ni SM Zr-4 oxidized sample (see Fig. 23).

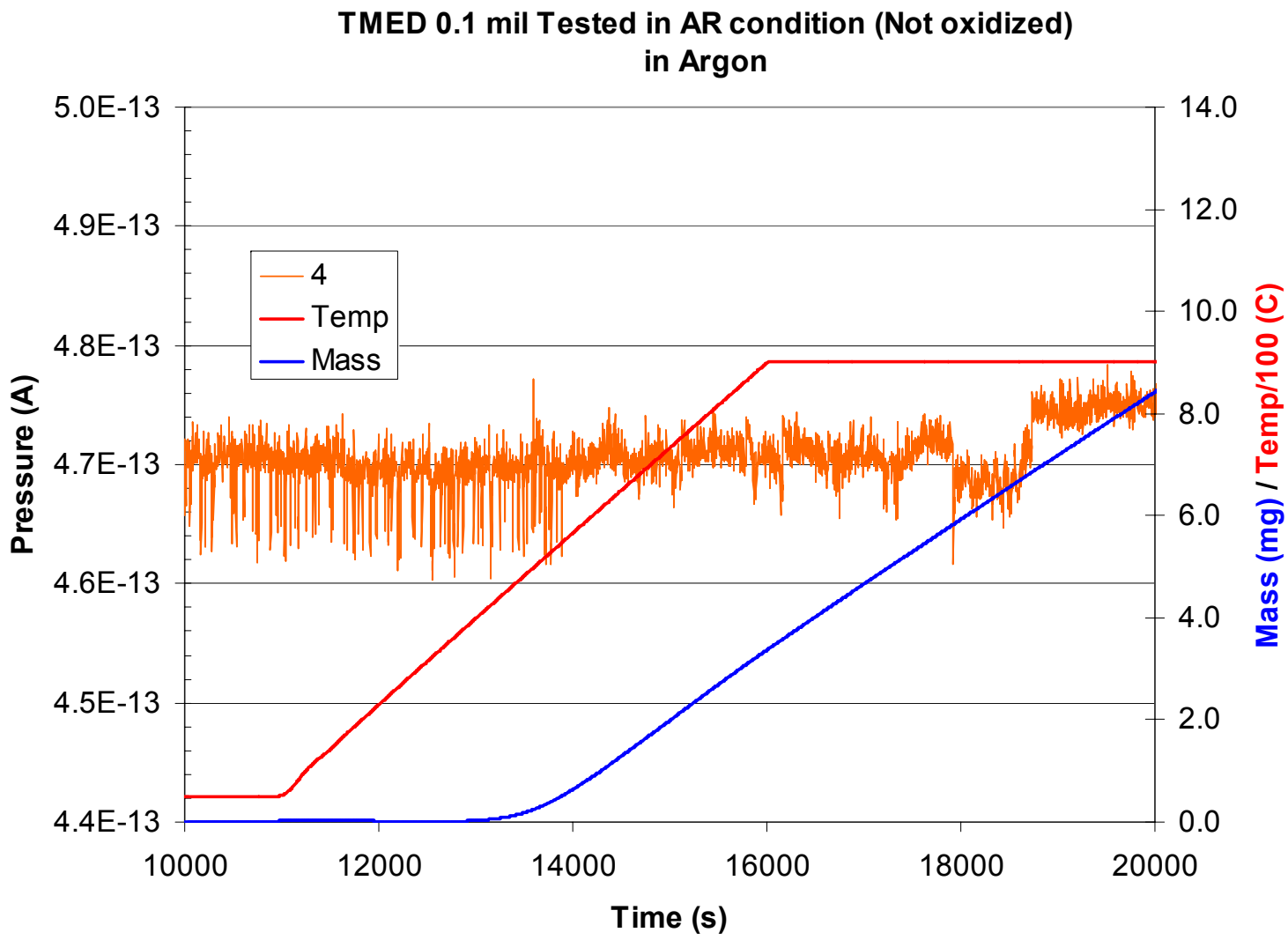

Figure 31. Thermogravimetric and Mass Spectroscopy data showing MS data for AMU 4 for 0.1 mil Ni SM Zr-4 As received sample (see Fig. 24).

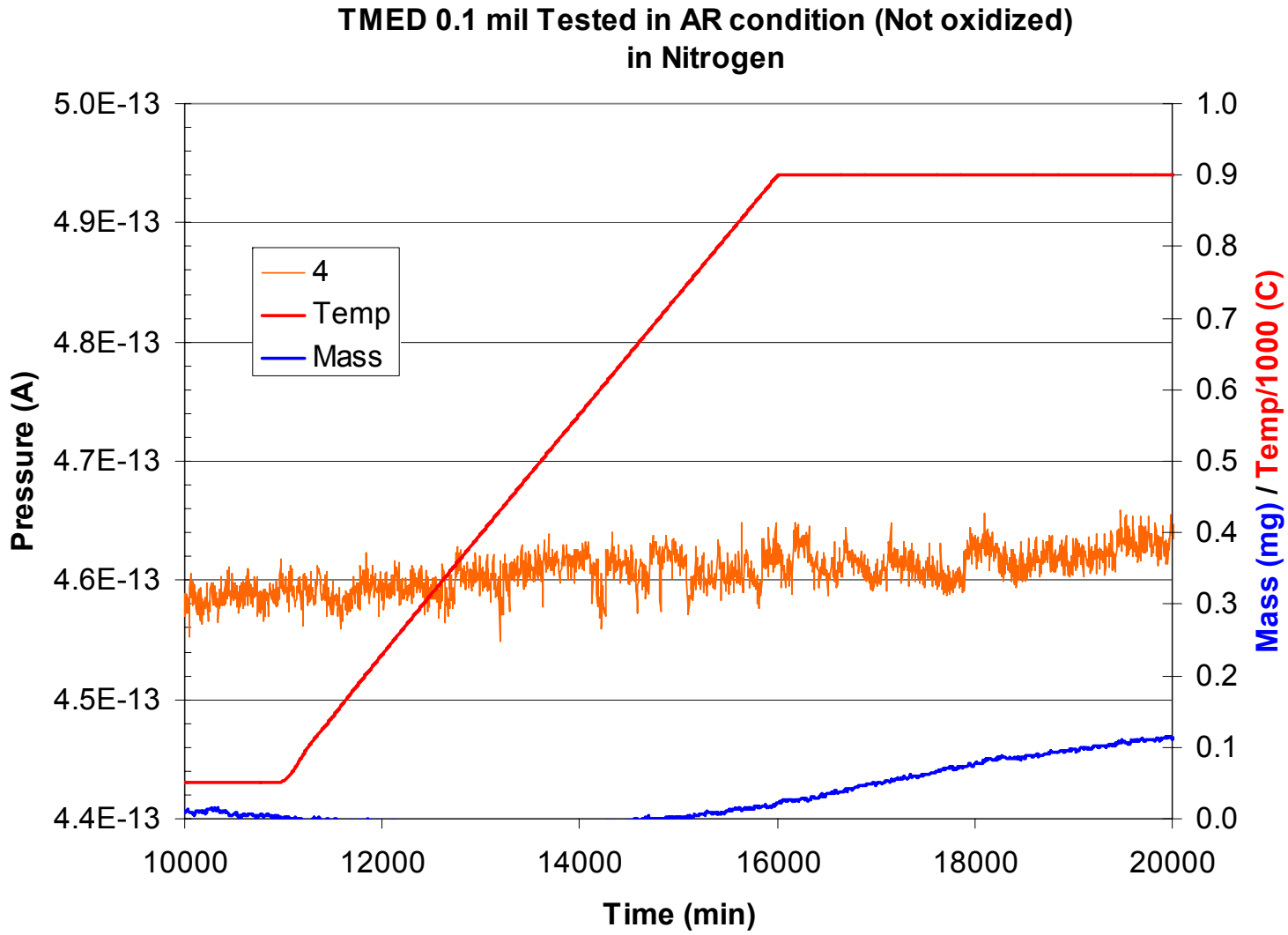

Figure 32. Thermogravimetric and Mass Spectroscopy data showing MS data for AMU 4 for 0.1 mil Ni SM Zr-4 as received sample tested in nitrogen.

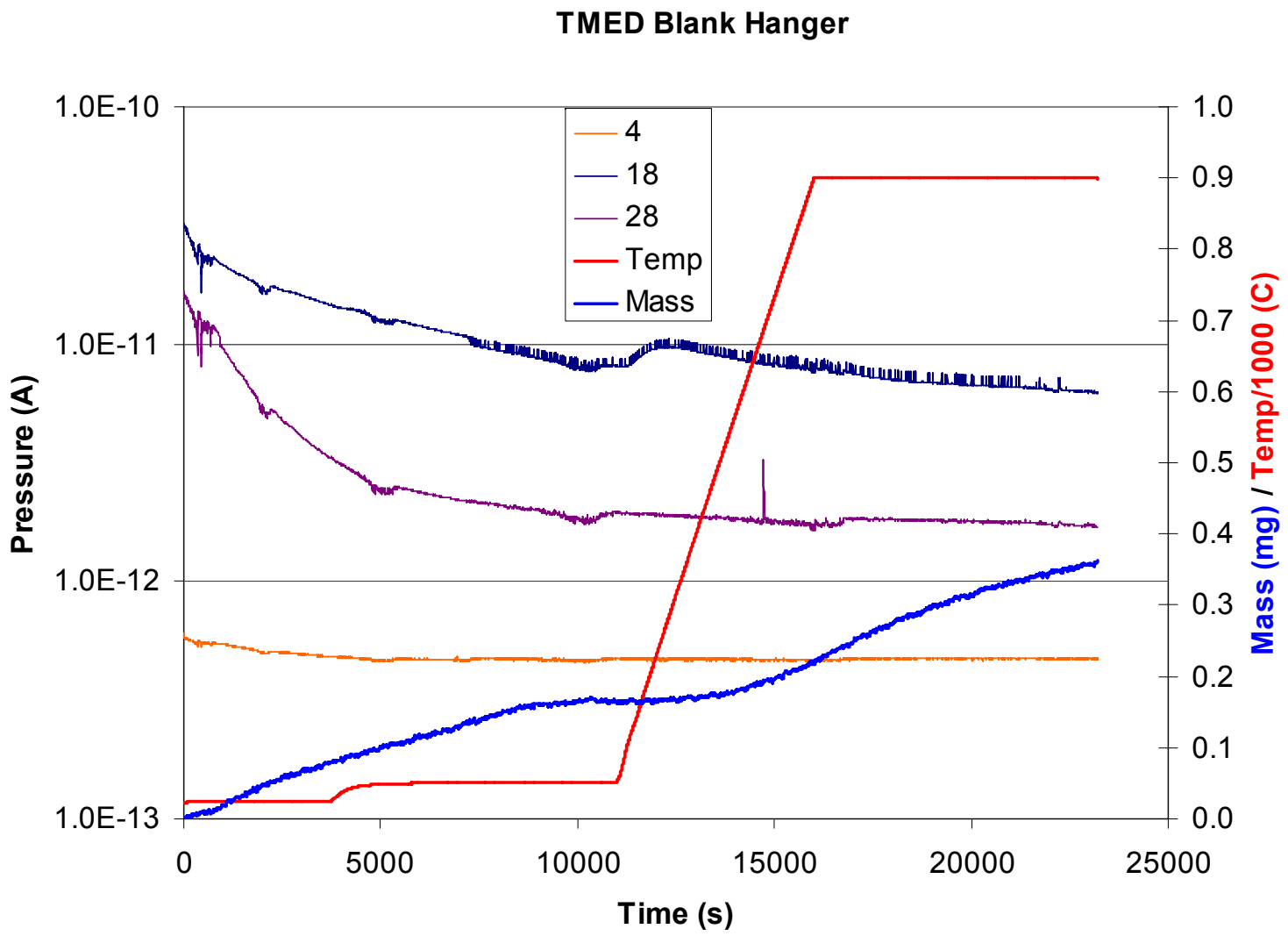

Figure 33. Mass Spectroscopy and TGA data for a blank. Note the presence of water and the flat AMU 4 peak with an amplitude of nominally 4.6 x 10^{-13}A.

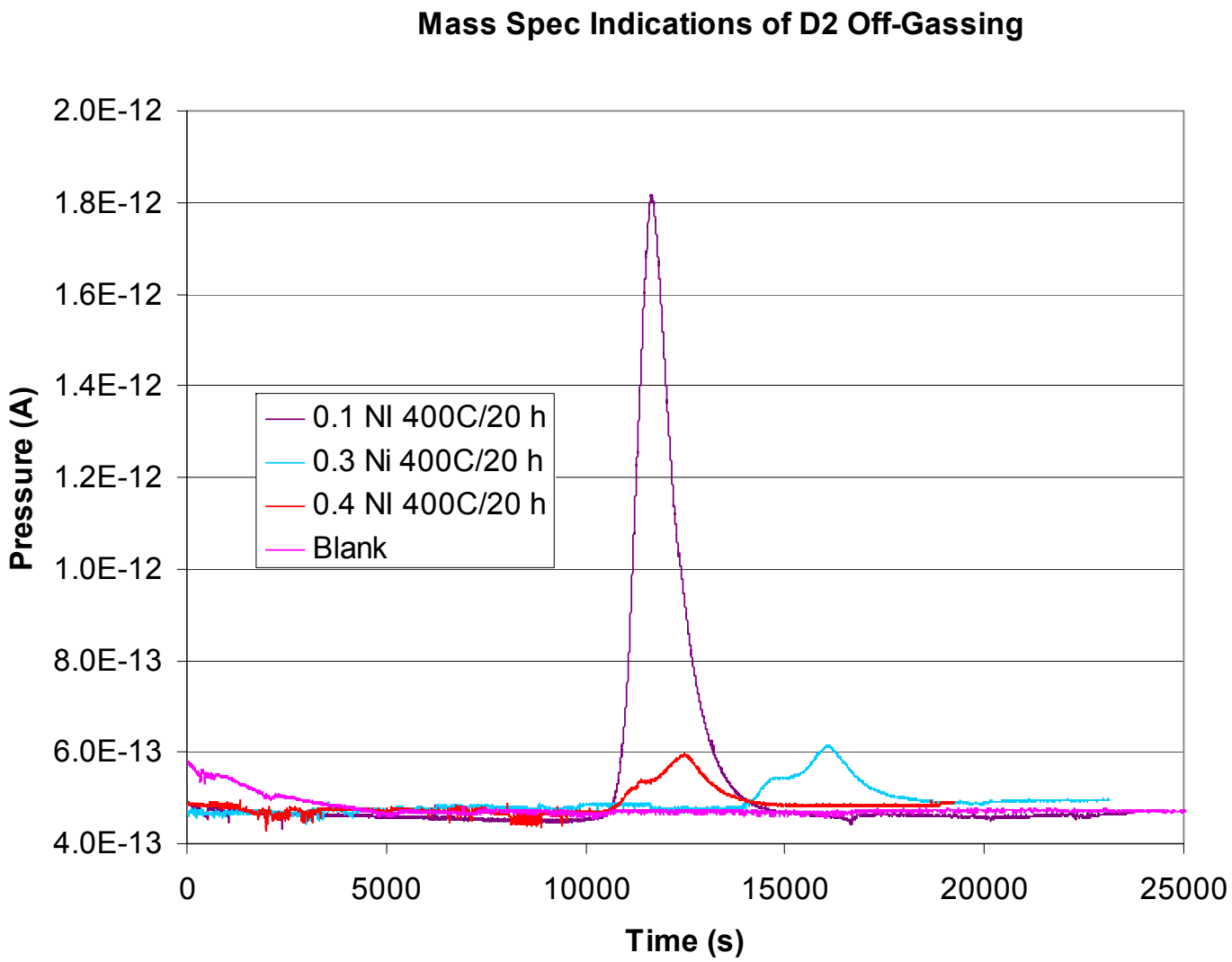

Figure 34. AMU 4 (deuterium) peaks that occurred during heating. Dwell times were different which accounts for the temporal displacement of the peaks.

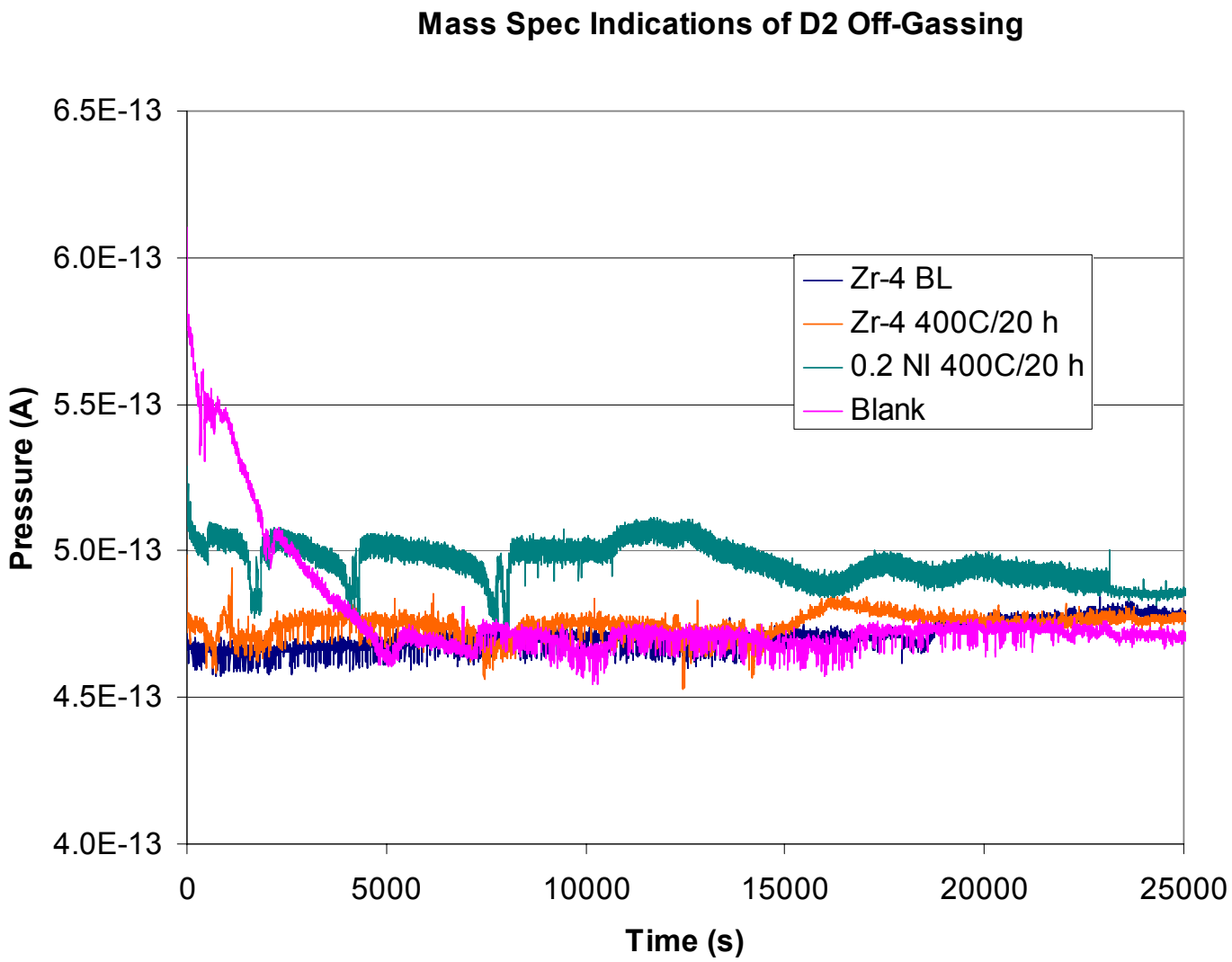

Figure 35. AMU 4 (deuterium) peaks that occurred during heating. Dwell times were different which accounts for the temporal displacement of the peaks. Note the significantly smaller peak heights compared to Figure 34.

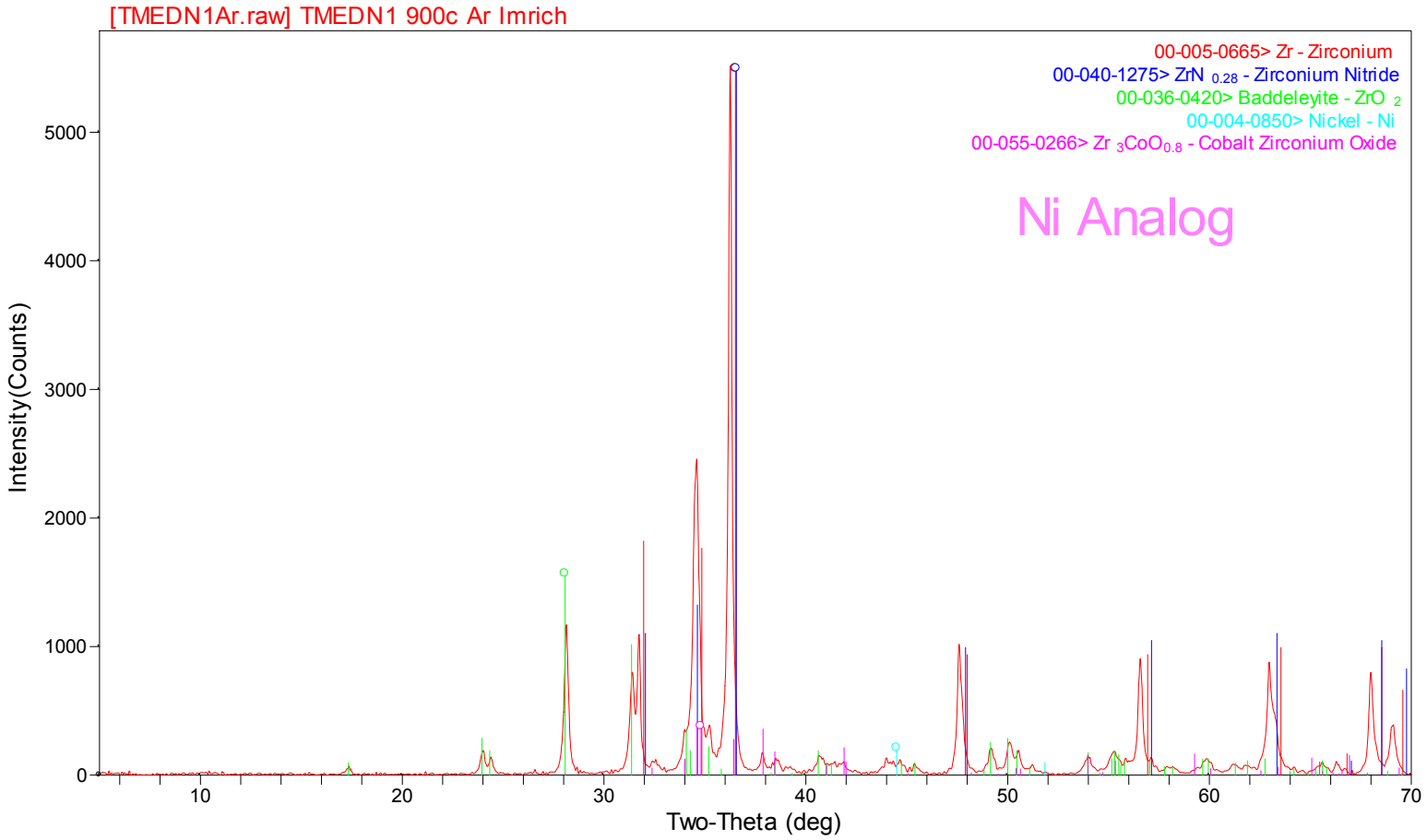

Figure 36. XRD results showing the presence of Zr, zirconium-nickel oxide, zirconium oxide, and possibly zirconium nitride, 0.1 mil Ni SM Zr-4 sample in the as received condition.

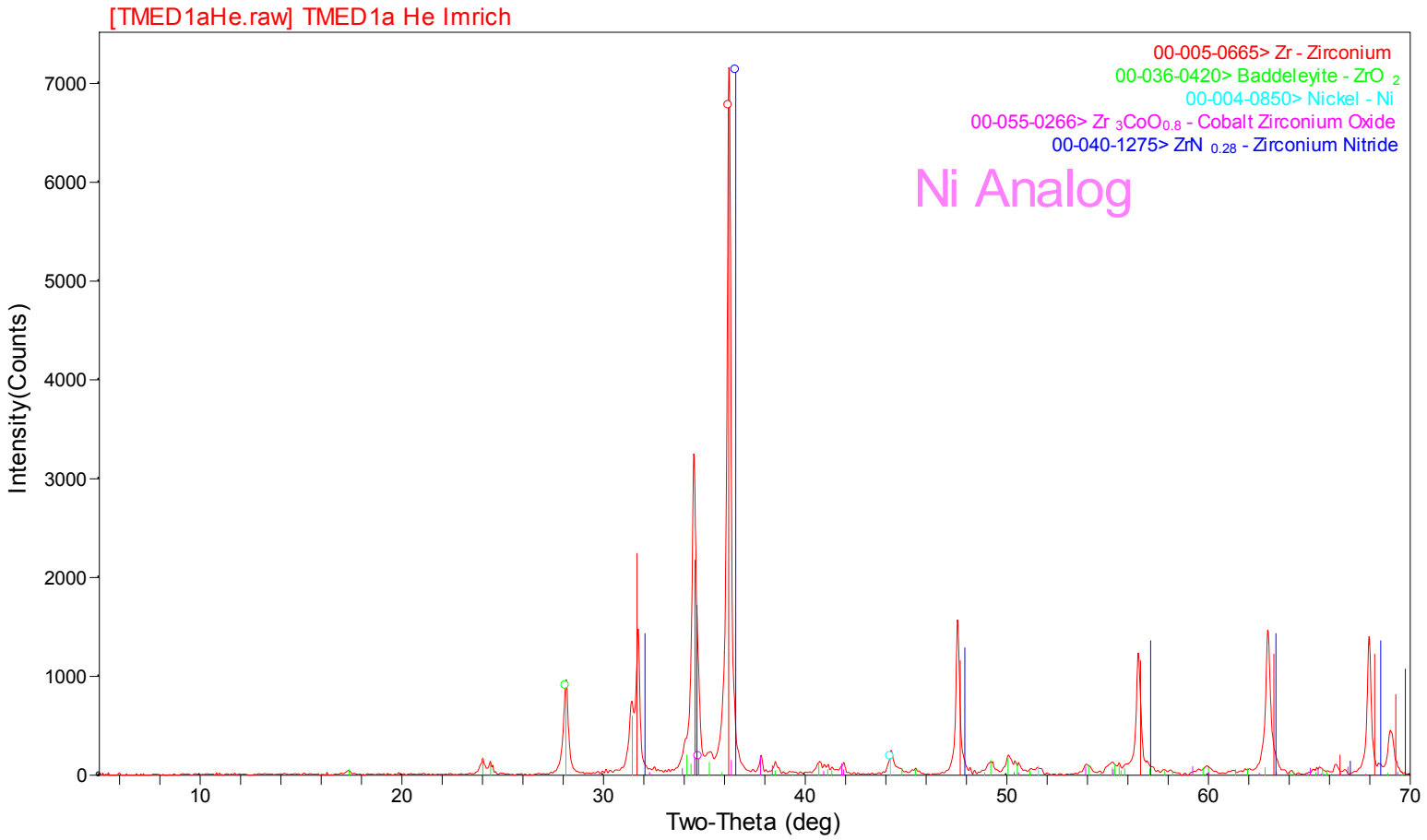

Figure 37. XRD results showing the presence of Zr, zirconium-nickel oxide, zirconium oxide, and possibly zirconium nitride, 0.1 mil Ni SM Zr-4 sample after being deuterium oxide tested at 400C for 20 hours.