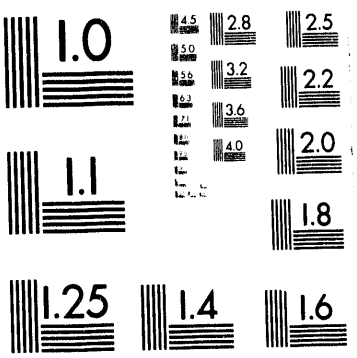

1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6
6.3
7.1

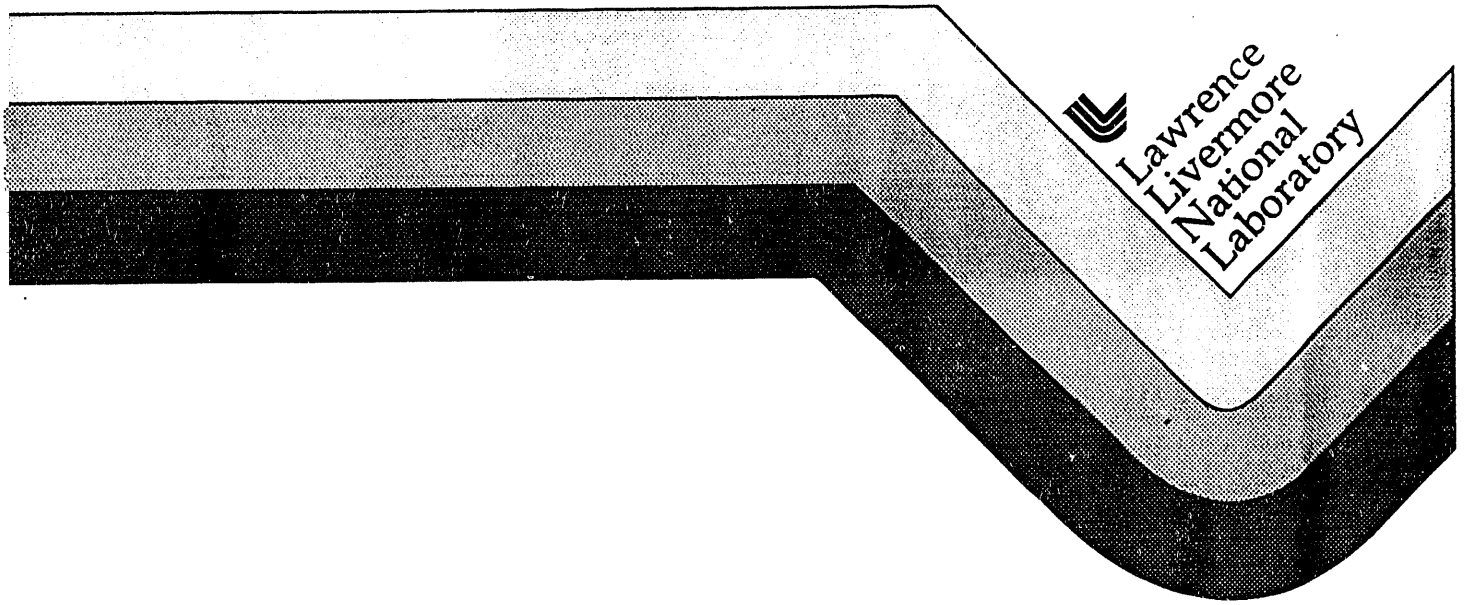
1 of 1

UCRL-CR-115799 SUM

Enhanced Thermal Capacity Aerogels Summary Report for FY 1993

Lawrence W. Hrubesh
Paul R. Coronado
John F. Poco

December 1993



DISCLAIMER

ENHANCED THERMAL CAPACITY AEROGELS

SUMMARY REPORT FOR 1993

CONTRACT #: A-26310D / L-1342

PREPARED FOR: NASA AMES RESEARCH CENTER
HIGH TEMPERATURE MATERIALS ENGINEERING
MOFFETT FIELD, CA 94035-1000

TECHNICAL MONITOR: Dr. Susan White

PRINCIPAL INVESTIGATOR: Lawrence Hrubesh
Chemistry and Material Science Department
Lawrence Livermore National Laboratory
Box 808 L-322
Livermore, CA 94550
OTHER INVESTIGATORS: Paul Coronado and John Poco

December 15, 1993

SUMMARY OF RESULTS:

In a continuation of work done previously, we have fabricated a set of silica aerogels and then chemically modified their internal surfaces for the purpose of inhibiting the effects of sintering at high temperatures. We performed surface nitridation of silica aerogels, i.e. the replacement of surface oxygen atoms with nitrogen atoms, by reacting ammonia gas with the silica surfaces at elevated temperatures. After pre-oxidizing the aerogels, we exposed three sets of samples to anhydrous ammonia gas under different processing conditions. Each set contained silica aerogels of three different densities, 0.07 g/cc, 0.16 g/cc, and 0.29 g/cc. The treated samples, together with companion untreated reference samples, were sent to NASA Ames Research Laboratory for high temperature testing.

We also fabricated two carbon aerogel cylinders, 7 cm diameter x 1.5 cm thick. These samples were also delivered to NASA Ames Research Laboratory for high temperature tests.

I. OBJECTIVE AND APPROACH

The objective of this work is to modify the surfaces of silica aerogels as a means to increase their thermal stability at high temperatures.

Our approach is to replace the bridging oxygen atoms at the surfaces of the silica aerogels with nitrogen atoms; then by further heat treatment, to form trigonal coordination of nitrogen atoms with the surface silicon atoms. When this is achieved, it should result in higher structural stability at elevated temperatures because of the lack of reactant sites available at the silica surfaces.

II. PROCEDURE

Aerogel fabrication:

We fabricated 4 silica aerogel samples at each of 3 different densities. The densities of each set are nominally; 70 mg/cc, 160 mg/cc, and 290 mg/cc. The samples were all cylinders with nominal dimensions of 2.5 cm diameter and 2.5 cm length. The silica aerogels were made using the following procedure:

A mole equivalent of tetramethoxysilane (TMOS) is mixed with 4 mole equivalents of distilled water and quantity of additional methanol calculated to give the targeted density. Ammonium hydroxide (200 µl/l) was added to the mixture and the entire solution was stirred for 30 minutes. The solutions were then poured into 25 ml pyrex glass beakers. The solutions gelled within 24 hours. All aerogels were supercritically dried in an autoclave at a nominal temperature of 290°C and a nominal pressure of 123 bars. Six aerogels for each density were set aside to be used as reference samples.

Nitridation:

Nitridation of the aerogel samples was done by exposing them to an atmosphere of anhydrous ammonia gas at elevated temperatures. The samples were placed in a quartz glass vessel which was attached to a vacuum system manifold. The vessel had an internal thermocouple located adjacent to the samples and it had clam-shell heaters on the outside. Different pretreatments were used for the aerogels before ammonia exposure according to the following schedule:

Sample #	Density (mg/cc)	Oxidation conditions	NH_3 exposure conditions
93-99-1-1	73	16hrs vac. @ 325°C, 6hrs. air @530°C, 16hrs vac. @ 650°C	750 torr NH3, 790°C, 8 hrs
93 -105-1-1	148	SAME	SAME
93-99-3-1	262	SAME	SAME
93-99-1-2	75	16hrs vac. @ 325°C, 6hrs. air @540°C, 4hrs vac. @ 770°C	575 torr NH3, 780°C, 1 hr x 3
93-105-1-2	153	SAME	SAME
93-99-3-2	268	SAME	SAME

Sample #	Density (mg/cc)	Oxidation conditions	NH_3 exposure conditions
93-99-1-3	72	16hrs vac. @ 325°C, 6hrs. air @550°C, 2hrs vac. @ 790°C	720 torr NH3, 790°C, 7.5hrs
93-105-1-3	155	SAME	SAME
93-99-3-3	268	SAME	SAME
93-99-1-4	78	16hrs vac. @ 325°C, 7hrs. air @545°C, 2hrs vac. @ 590°C	550 torr NH3, 600°C, 24hrs x 3
93-105-1-4	150	SAME	SAME
93-99-3-4	260	SAME	SAME
93-99-1-5	75	16hrs vac. @ 325°C, 6hrs. air @535°C, 2hrs vac. @ 650°C, 2nd oxidation 15hrs. @500°C	630 torr NH3, 800°C, 1hr x 3
93-105-1-5	147	SAME	SAME
93-99-3-5	255	SAME	SAME
93-99-1-6	76	16hrs vac. @ 325°C, 10hrs. air @570°C, 2hrs vac. @ 565°C, 7hrs vac. @ 800°C	540 torr Ar, 800°C, 2hrs
93-105-1-6	153	SAME	SAME
93-99-3-6	266	SAME	SAME

Several of the aerogels cracked during the above procedures and all aerogels show a black coloration during the heating cycle. Most samples became clear again during the oxidation step.

III. ANALYSIS

Density and Volume Change

The weight and volume of the nitrided silica aerogel samples were measured immediately upon removal from the vessel. The weight gain was then measured for approximately 30 hours while the samples were continuously exposed to room air having an average relative humidity of 63%. The density data for the samples are given below. Typical weight gain and % weight gain versus time curves are shown in figures 1,2, 3, and 4 for representative samples from each set.

Sample #	Density (mg/cc)			Volume shrinkage (%)
	Starting	After Nitriding	After air exposed	
93-99-1-1	73	115	124	44.9
93-105-1-1	148	192	196	33.4
93-99-3-1	262	340	341	18.7
93-99-1-2	75	119	121	47.5
93-105-1-2	153	188	193	28.8
93-99-3-2	268	292	300	17.7

93-99-1-3	72	174	176	63.8
93-105-1-3	155	213	217	36.9
93-99-3-3	268	319	325	25.5
93-99-1-4	78	116	118	41.3
93-105-1-4	150	171	176	23.4
93-99-3-4	260	308	319	24.4
93-99-1-5	75	103	105	36.8
93-105-1-5	147	179	185	28.8
93-99-3-5	255	292	302	22.4
93-99-1-6	76	105	106	37.6
93-105-1-6	153	177	178	24.9
93-99-3-6	266	288	290	18.0

Carbon, Hydrogen and Nitrogen Content

We analyzed representative aerogel samples to determine the quantitative change in the elements on the surfaces of the silica aerogels due to the nitridation treatment. The following lists the weight percents of the elements, carbon, hydrogen, and nitrogen for aerogels (corrected for air within the aerogels) that was nitrided at 790°C compared with a non-treated aerogel. The decrease in the carbon and hydrogen content of the heat treated samples is evident, as is the increased quantity of nitrogen for the nitrided samples. However, other analyses are required to determine the form of the nitrogen on the surfaces, i.e. whether the nitrogen has replaced surface oxygens and whether it is trigonally bonded or not.

Sample #	Type	% Carbon	% Hydrogen	% Nitrogen
92-133-2A	Nitrided @ 750°C	0.02	0.31	0.35
92-133-2B	Untreated	5.01	1.80	0.05

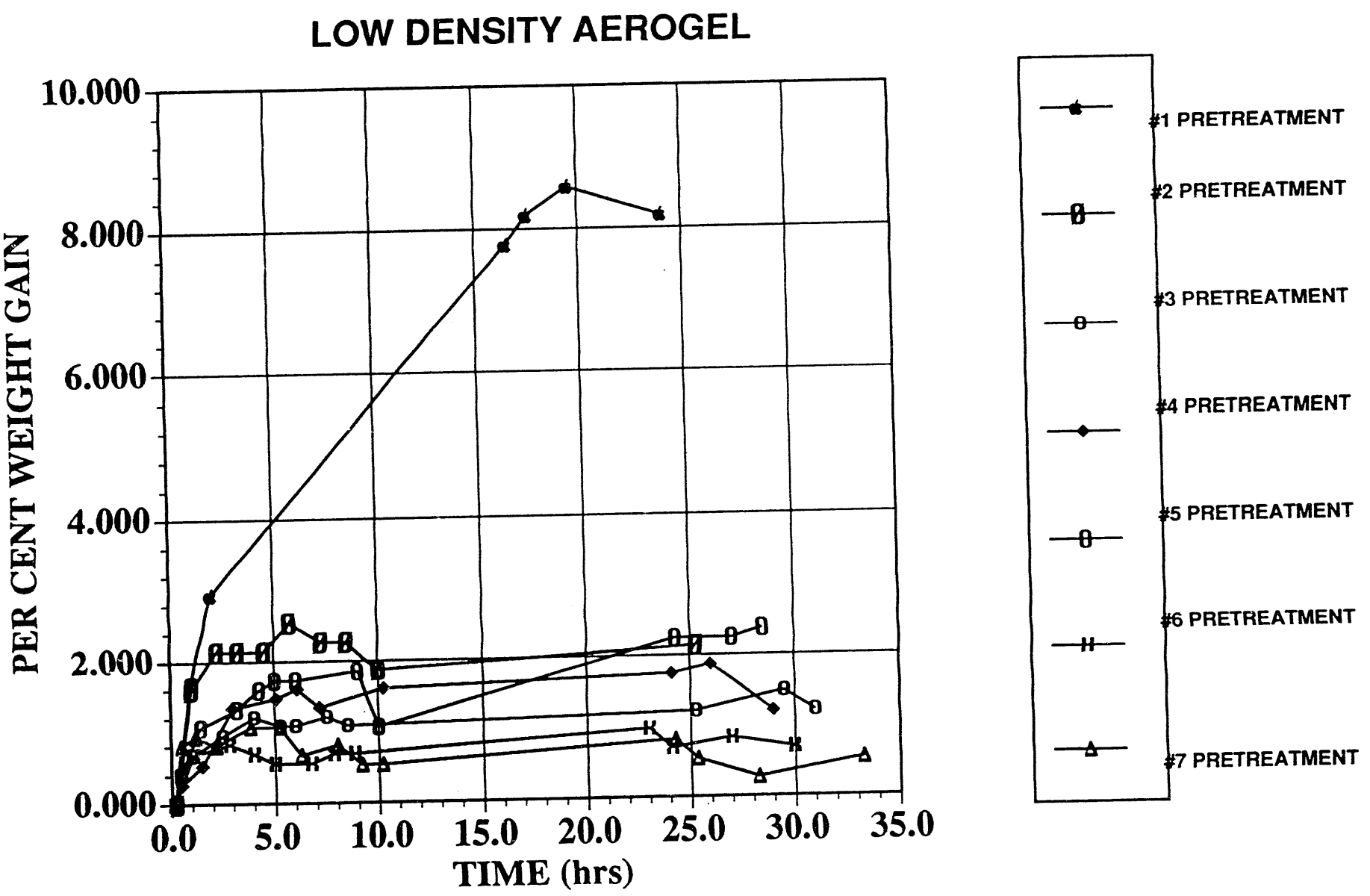
IV. SUMMARY

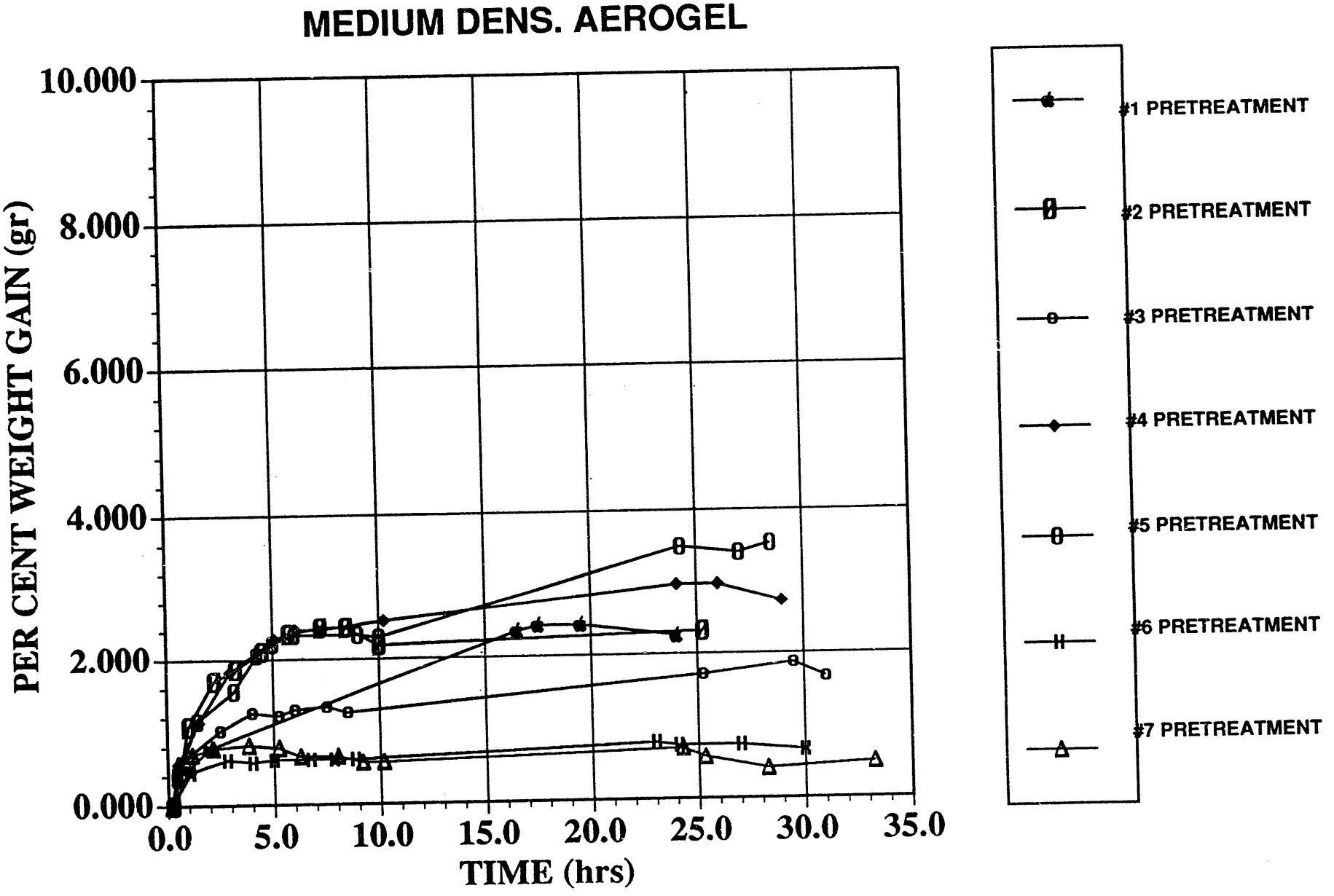
Several sets of silica aerogel samples were surface treated at elevated temperatures to induce nitrogen replacement for oxygen atoms on the surfaces. These samples, together with the untreated reference samples, are being provided to NASA - Ames Laboratory for further measurements to determine the extent to which the nitriding of the surfaces raises the temperature for the onset of shrinkage due to sintering.

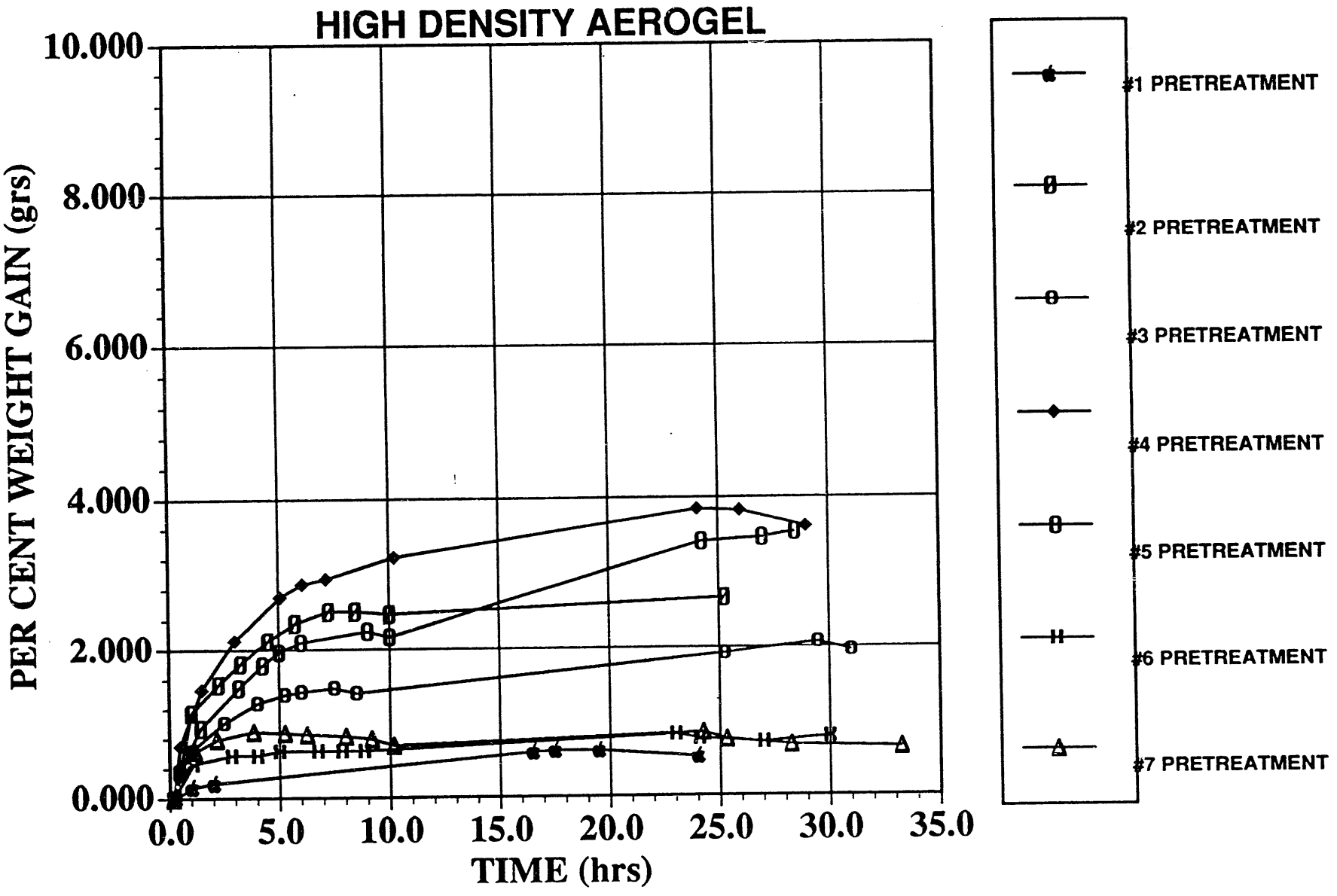
	Label	A	B	C	D	E	F	G	H	I	J	K	L
Label	JP SAMPLE #	93-99-1-1	93-105-1-1	93-99-3-1	TIME (hrs)	93-99-1-2	93-105-1-2	93-99-3-2	TIME (hrs)		93-99-1-3	93-105-1-3	93-99-3-3
1	STARTING DENSITY	73 mg/cc	148 mg/cc	262 mg/cc		75 mg/cc	153 mg/cc	268 mg/cc			72 mg/cc	155 mg/cc	268 mg/cc
2	STARTING VOLUME	11.873 cc	18.853 cc	19.380 cc		11.488 cc	18.027 cc	19.08 cc			11.812 cc	18.339 cc	19.08 cc
3	ENDING DENSITY	115 mg/cc	192 mg/cc	340 mg/cc		119 mg/cc	188 mg/cc	292 mg/cc			174 mg/cc	213 mg/cc	319 mg/cc
4	ENDING VOLUME	6.506	12.666	13.298		6.301 cc	12.835 cc	15.687 cc			4.272 cc	11.575 cc	14.214 cc
5	STARTING WEIGHT	0.861 g	2.789 g	5.078 g		0.862 g	2.766 g	5.129 g			0.853	2.833	5.104
6	ENDING WEIGHT	0.746	2.429	4.524		0.748 g	2.417 g	4.58 g			0.742	2.461	4.54
7	% weight change	13.400	12.900	10.900		13.2	12.6	10.7			13%	13%	11%
8													
9			conditions (1)				conditions (2)					conditions (3)	
10	CONDITIONS (1)	rough vac 16	hours @ 325C			rough vac 16	hours @325C				rough vac 16 hours @325C		
11		oxidation 6 ho	urs in air @ 53	0C		oxidation 6 ho	urs in air 540C				oxidation 6 hours in air 550C		
12		Hard Vac 16 h	ours @ 650-770C			Hard Vac 4 hou	rs @ 772C				HV 2hrs. 730C	-770C	
13		NH3 750 torr	8 hours @790C			NH3 575 torr	780C 1 hour 3	times			NH3 720 torr	7.5 hrs. 790C	
14													
15													
16	WEIGHT GAIN %	0.000	0.000	0.000	0.3	0	0	0	0.25		0	0	0
17		1.740	0.500	0.150	1.0	1.6	1.08	1.15	1		0.4	0.5	0.35
18	GOT WET	2.950	0.780	0.200	2.0	2.14	1.7	1.53	2.25		0.67	0.69	0.64
19		7.780	2.350	0.600	16.5	2.14	1.86	1.81	3.25		0.94	1.02	1.01
20		8.180	2.430	0.620	17.5	2.14	2.11	2.12	4.5		1.21	1.26	1.28
21		8.580	2.430	0.620	19.5	2.54	2.36	2.36	5.75		1.08	1.22	1.39
22		8.180	2.260	0.530	24.0	2.27	2.44	2.51	7.25		1.08	1.3	1.43
23						2.27	2.44	2.51	8.45		1.21	1.34	1.48
24						1.87	2.19	2.47	10		1.08	1.26	1.41
25						2.14	2.32	2.66	25.25		1.21	1.71	1.92
26											1.48	1.87	2.07
27											1.21	1.67	1.96
28													
29													
30													
31													
32													
33													
34													
35													
36													
37													
38													
39													
40													
41													
42													
43													
44													
45													

	M	N	O	P	Q	R	S	T	U	V	W	X	Y	Z
Label	TIME (hrs)		93-99-1-4	93-105-1-4	93-99-3-4	TIME(hrs)		93-99-1-5	93-105-1-5	93-99-3-5	TIME (hrs)		93-99-1-6	93-105-1-6
1			78 mg/cc	150 mg/cc	260 mg/cc			75 mg/cc	147 mg/cc	255 mg/cc			76 mg/cc	153. mg/cc
2			10.986 cc	18.679 cc	19.718 cc			11.589 cc	19.051 cc	20.175 cc			11.132	18.27
3			116 mg/cc	171 mg/cc	308 mg/cc			103 mg/cc	179 mg/cc	292 mg/cc			105 mg/cc	177 mg/cc
4			6.449 cc	14.313 cc	14.914 cc			7.33	13.573	15.651			6.943	13.729
5			0.86	2.80	5.13			0.869 grams	2.798 grams	5.135 grams			0.848 gr	2.792 gr
6			0.75	2.45	4.60			.755 grams	2.432 grams	4.571 grams			0.730 gr	2.426 gr
7			12.6	12.40	10.40			13.1	13.1	11			13.9	13.1
8														
9				conditions (4)					conditions (5)					conditions (6)
10			rough vac 16 hours @ 325C					rough vac 16 hours @ 325C					rough vac 16 hours @ 328C	
11			oxidation 7 hours in air 545C					oxidation 6 hours in air 535C					oxidation 10 hours in air 570C	
12			HV 2 hrs. 590C					HV 2 hrs. 650C					HV 2 hrs 565C	
13			NH3 550 torr	600C 24 hours	3 times			NH3 627 torr @	800C to 600C 3	times 1 hr each			HV 7 hrs @ 800C	
14													Argon 540 torr	2 hrs @ 800C
15														
16	0.25		0.00	0.00	0.00	0.17		0	0	0	0.17		0	0
17	0.5		0.27	0.57	0.70	0.50		0.4	0.37	0.35	0.42		0.68	0.45
18	1		0.53	1.14	1.46	1.50		1.06	1.15	0.94	1.42		0.82	0.62
19	2.5		1.34	1.83	2.13	3.00		1.32	1.56	1.49	3.17		0.68	0.58
20	4		1.47	2.28	2.70	5.10		1.59	2.06	1.79	4.25		0.55	0.62
21	5.25		1.60	2.41	2.87	6.10		1.72	2.22	1.97	5.00		0.55	0.62
22	6		1.34	2.41	2.94	7.17		1.72	2.34	2.1	6.00		0.68	0.62
23	7.5		1.60	2.53	3.22	10.25		1.85	2.34	2.25	9.00		0.68	0.62
24	8.5		1.74	2.98	3.85	24.08		1.06	2.3	2.17	10.00		0.96	0.78
25	25.25		1.87	2.98	3.83	26.00		2.25	3.5	3.41	24.25		0.68	0.74
26	29.5		1.20	2.73	3.61	29.00		2.25	3.41	3.46	27.00		0.82	0.74
27	31							2.38	3.54	3.54	28.50		0.68	0.66
28														
29								samples dark	conditions (7)					
30								oxidation 2nd time	@500C 15 hours					
31														
32								0	0	0	0.17			
33								0.8	0.57	0.41	0.5			
34								0.93	0.7	0.63	1.17			
35								0.8	0.78	0.79	2.17			
36								1.06	0.82	0.89	3.83			
37								1.06	0.78	0.87	5.25			
38								0.66	0.66	0.85	6.25			
39								0.8	0.66	0.83	8			
40								0.53	0.57	0.79	9.17			
41								0.53	0.57	0.7	10.17			
42								0.8	0.7	0.85	24.25			
43								0.53	0.57	0.76	25.33			
44								0.27	0.41	0.68	28.25			
45								0.53	0.49	0.65	33.25			

	AA	AB
Label	93-99-3-6	TIME (hrs)
1	266 mg/cc	
2	19.357	
3	288 mg/cc	
4	15.874	
5	5.142 gr	
6	4.570 gr	
7	11.1	
8		
9		
10		
11		
12		
13		
14		
15		
16	0	0.15
17	0.46	1.08
18	0.57	2.83
19	0.57	4
20	0.63	5
21	0.63	6.75
22	0.63	7.83
23	0.63	8.83
24	0.83	23
25	0.77	24.08
26	0.72	27
27	0.79	30
28		
29		
30		
31		
32		
33		
34		
35		
36		
37		
38		
39		
40		
41		
42		
43		
44		
45		


LOW DENSITY AEROGEL
PER CENT WEIGHT GAIN
10.000
8.000
6.000
4.000
2.000
0.000
0.0
5.0
10.0
15.0
20.0
25.0
30.0
35.0
TIME (hrs)
#1 PRETREATMENT
#2 PRETREATMENT
#3 PRETREATMENT
#4 PRETREATMENT
#5 PRETREATMENT
#6 PRETREATMENT
#7 PRETREATMENT


MEDIUM DENS. AEROGEL
PER CENT WEIGHT GAIN (gr)
10.000
8.000
6.000
4.000
2.000
0.000
0.0
5.0
10.0
15.0
20.0
25.0
30.0
35.0
TIME (hrs)
#1 PRETREATMENT
#2 PRETREATMENT
#3 PRETREATMENT
#4 PRETREATMENT
#5 PRETREATMENT
#6 PRETREATMENT
#7 PRETREATMENT


HIGH DENSITY AEROGEL
PER CENT WEIGHT GAIN (grs)
10.000
8.000
6.000
4.000
2.000
0.000
0.0
5.0
10.0
15.0
20.0
25.0
30.0
35.0
TIME (hrs)
#1 PRETREATMENT
#2 PRETREATMENT
#3 PRETREATMENT
#4 PRETREATMENT
#5 PRETREATMENT
#6 PRETREATMENT
#7 PRETREATMENT

DATE
FILMED
4/22/94
END