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71 H. C. STARCK, INC.

FULL NAME(S) OF INVENTOR(S)

72 MALEN, Richard; KUMAR, Prabhat

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54 CAPACITOR-GRADE LEAD WIRES WITH INCREASED TENSILE STRENGTH AND HARDNESS

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FOR ABSTRACT SEE THE NEXT SHEET

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(71) Applicant (*for all designated States except US*): H.C. STARCK INC. [US/US]; 45 Industrial Place, Newton, MA 02161-1951 (US).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): MALEN, Richard [US/US]; 1 East Main Street, Ayer, MA 01432-1605 (US). KUMAR, Prabhat [US/US]; 31 Pinewood Drive, Framingham, MA 01701-7656 (US).

(74) Agents: VAN EYL, Diderico et al.; Bayer Corporation, 100 Bayer Road, Pittsburgh, PA 15205-9741 (US).

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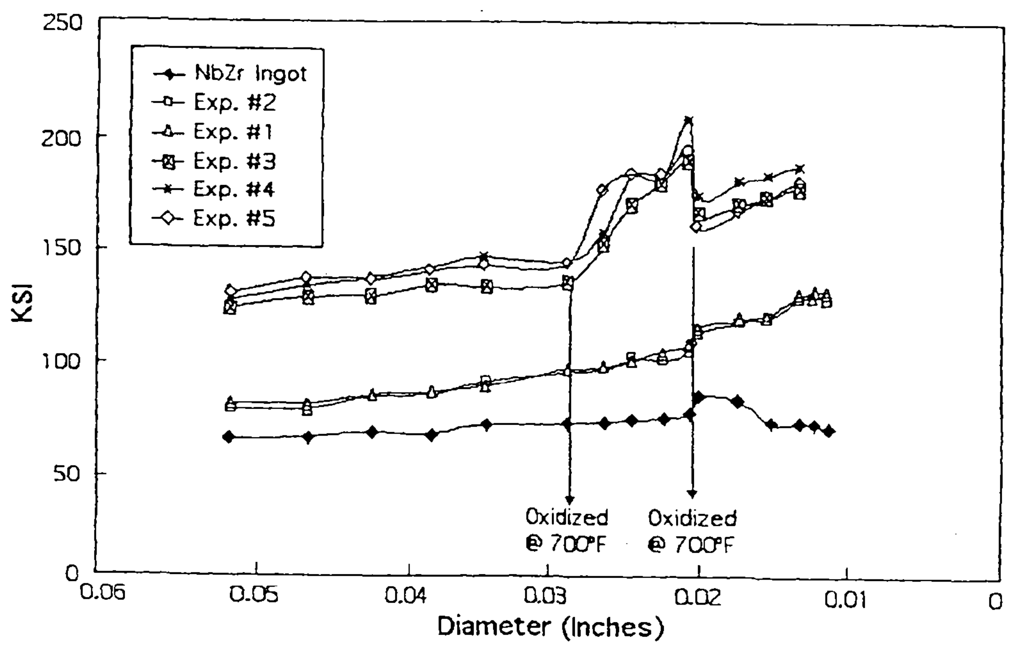

(57) Abstract: A capacitor-grade wire made from powder metallurgy containing at least niobium and silicon, wherein the niobium is the highest weight percent metal present in the niobium wire. The wire having a controlled tensile strength at finish diameter exceeds the strength of capacitor-grade wire formed by ingot metallurgy. Also, the powder metallurgy wire hardness exceeds capacitor-grade wire formed from ingot metallurgy with electrical leakage meeting the specifications normally applied to capacitor grade tantalum, niobium or niobium-zirconium lead wire at sinter temperatures of about 1150°C and above.

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CAPACITOR-GRADE LEAD WIRES WITH INCREASED TENSILE STRENGTH AND HARDNESS

BACKGROUND OF THE INVENTION

The invention relates generally to capacitor lead wires, more particularly to niobium lead wires usable with anode compacts of tantalum or niobium. The invention includes niobium powder metallurgy derived lead wires of niobium doped with silicon, preferably having improved strength and hardness without significant detriment to electrical leakage rating of the wire.

Niobium and niobium alloy lead wires with melt source derivation have been used as capacitor lead wires. Pure niobium wires of melt process origin have low electrical leakage at sintering temperatures of 1150°C and above. However the wires are limited in tensile strength and hardness, which make them difficult to work with; this results in low production through put when bonding the wires to the capacitor anode compacts and/or in the course of sintering the compact or prolysis of solid electrolyte with the lead wire attached. Niobium alloys, such as niobium-zirconium have better tensile strength then pure niobium wires of melt process origin and acceptable electrical leakage above 1150°C. However above 1050°C zirconium diffuses off the wire and contaminates the anode, making it unacceptable as a capacitor lead wire.

It is an object of the present invention to improve chemical, mechanical, metallurgical, and functional consistency of capacitor grade lead wires.

It is a further object of the present invention to reduce sintering and bonding problems.

It is yet a further object of the present invention to improve niobium wire to overcome the above-described disadvantages without significantly impacting the electrical properties of the wire and wire-anode assembly.

SUMMARY OF THE INVENTION

The invention relates to a process for making a capacitor grade silicone-doped niobium lead wire comprising (a) forming a low oxygen niobium powder by hydriding a niobium ingot or a niobium bar and grinding or milling the ingot or the bar, and thereby making a powder having a Fisher Average Particle Diameter particle size range of less than about 150 microns, (b) dehyriding the powder, and optionally deoxidizing the powder, forming a low oxygen niobium powder, (c) blending the low oxygen niobium powder with a silicon additive powder and compacting the powder by cold isostatic pressing to a bar; (d) thermomechanically processing the bar into a rod, and (e) subjecting the rod to a combination of rolling and cold drawning steps, and forming the silicon doped wire. The invention also relates to a method made from such a process.

The present invention includes a niobium wire made from powder metallurgy (P/M), containing a silicon additive of less than about 600 ppm. Generally, the amount of silicon ranges from about 150 to about 600 ppm. Preferably, the amount of silicon ranges from about 150 to 300 ppm. The invention imparts a controlled, higher mechanical tensile strength in the niobium wire at finish diameter that exceeds capacitor-grade wire formed from niobium and niobium-zirconium alloys derived directly from ingot metallurgy (I/M). Preferably too the P/M source niobium has oxygen content below 400 ppm, even when silicon is added in an oxide form. The P/M derived niobium, and niobium-silicon wires also have increased hardness that exceeds hardness of capacitor-grade wire of I/M niobium and niobium-zirconium wires and electrical leakage within current specifications at sinter temperatures of about 1150°C and above, or about 1250 and above. The P/M source material if sintered at well below about 1150°C or 1250 °C and above, and/or attached to anode compacts sintered below about 1150°C or below 1250 °C would have higher leakage. But at about 1150°C or 1250°C and above, the differences become minimal.

It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are intended to provide further explanation of the present invention as described.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a chart of the ultimate tensile strength as a function of wire diameter of select niobium and niobium alloy wire of the present invention derived from powder metallurgy compared to niobium and niobium alloy wire derived from ingot metallurgy;

Fig. 2 is a chart of electrical DC leakage as a function of sintering temperature of select niobium and niobium alloy wire of the present invention derived from powder metallurgy compared to niobium and niobium alloy wire derived from ingot metallurgy;

Fig 3A-3F are side and front views of examples of capacitor lead wires bonded to anode compacts; and

Fig. 4 is a chart of electrical DC leakage as a function of sintering temperature of select niobium and niobium alloy wire of the present invention derived from powder metallurgy compared to niobium and niobium alloy wire derived from ingot metallurgy.

DETAILED DESCRIPTION OF THE INVENTION

One of the preferred embodiments of the invention is a lead wire of silicone-doped niobium made as follows. Niobium powders are formed by hydriding an ingot or bar of niobium and grinding or otherwise milling the ingot or bar to create a powder at a size range of less than 150 microns FAPD (Fisher Average Particle Diameter), dehyriding and deoxidating. The hydride-grind process as disclosed in U.S. 3,295,951 of Fincham et al and the deoxidation (with a combined dehydriding deoxidation) is described in U.S. Patent 6,261,337 of Kumar, incorporated herein by reference in their entirety, both said patents are of common assignment with this application and Mr. Kumar as a joint inventor of the present invention. The niobium powder preferably is attained with an oxygen level below 400 ppm, preferably below 200 ppm. A silicon additive powder is blended with the low oxygen niobium powder, compacted by cold isostatic pressing (at up to 60 KSI) to a preform billet for extrusion or sinter bar preferably yeilding a bar approximately 1.3 inches diameter. The bar is thermomechanically processed to a rod. The rod is then rolled (or swaged) and cold drawn, typically with a schedule of reductions and intermediate anneals as follows:

Annealed at 2500°F for 1.5 hours;
Rolled to 0.440 inches diameter;
Annealed at 2500°F for 1.5 hours;
Reduced to 0.103 inches diameter;
Drawn to 0.0346 inches diameter wire;
Drawn to a finish diameter.

Stated in general terms, the rod can be rolled (or swaged) and cold drawn, typically with a schedule of reductions and intermediate anneals as follows:

Annealed at a temperature ranging from about 2100°F to about 2700°F for a time ranging from about 0.5 hours to about 2.0 hours;

Rolled from a diameter ranging from about 1 inch to about 0.25 inches diameter;

Annealed at a temperature ranging from about 2100 to about 2700°F for a time ranging from about 0.5 hours to about 2.0 hours;

Reduced from about 1 inch to about to 0.075 inches diameter;

Drawn to a finish diameter.

The diameter of the wire made in accordance to the invention can range from about 0.005 inches to about 0.1 inches. The wire of the present invention can contain other additional ingredients such as other metals or ingredients typically added to niobium metal, such as tantalum, zirconium, titanium, or mixtures thereof. The types and amounts of these additional ingredients can be the same as those used with conventional niobium and would be known to those skilled in the art. TABLE 1 below lists the chemistry of the specimens used in certain Experiments 1-5 of silicon doped niobium wire of powder metallurgy origin as reduced to 0.5 inch diameter and 0.103 inch diameter.

TABLE 1

PPM		C	O	N	Mg	Al	Si	Ti	Cr	Fe	Ni	Cu	Zr	Mo	Ta	W
Experiment #1	1/2"	88	646	47	114	20	25	20	108	655	157	10	10	20	1388	200
Experiment #2	1/2"	90	301	42	106	20	158	20	99	574	133	16	10	20	8374	200
Experiment #3	1/2"	54	322	60	120	0.5	13	6.1	45	225	44	4	5	1	3000	5
Experiment #4	1/2"	142	358	60	120	1.1	161	5.3	50	255	53	3.5	5	1	10000	7.1
Experiment #5	1/2"	58	329	72	95	2.7	306	5.5	45	230	53	7	5	1	20000	7.5
Experiment #1	.103"	63	173	31	110	2	23	2	140	500	130	4	5	11	1000	55
Experiment #2	.103"	71	180	28	105	3	163	2	150	675	150	6.4	5	11	10000	85
Experiment #3	.103"	57	262	49	85	5.2	12	7.5	65	100	55	1.9	5	1	5000	6.8
Experiment #4	.103"	79	291	52	100	4.1	162	6.1	63	130	65	2.2	5	1	10000	5.7
Experiment #5	.103"	61	282	59	80	2.8	294	4.9	63	70	55	1.9	5	1	10000	6.5

Wires were prepared from the silicon master blends presented in Experiments 1-5 of TABLE 1, and sample were taken at various size milestones and tested for tensile strength and hardness (Rockwell hardness B scale, HRB). I/M derived niobium-zirconium wires (prior art) were also tested similarly.

TABLE 2

	Prior Art		Nb PM		Nb PM		Nb PM		Nb PM		Nb PM	
	NbZr Ingot		Exp. #1 (25 ppm)		Exp. #2 (150 ppm)		Exp. #3 (10 ppm)		Exp. #4 (150 ppm)		Exp. #5 (300 ppm)	
Size	Hardness	Tensil	Hardness	Tensil	Hardness	Tensil	Hardnes s	Tensil	Hardness	Tensil	Hardness	Tensil
In	HRB	KSI	HRB	KSI	HRB	KSI	HRB	KSI	HRB	KSI	HRB	KSI
0.6	83.7		73		74.3		75.7		76.5		80.2	
0.42	82.4		74.9		73.2		36.7		39.7		43.1	
0.266	89.8		74.4		71		74.3		76.9		79.1	
0.166	89.1		74.5		76.6		79.9		81		81.1	
0.107	87.7		72		81		82		82.5		84.7	
0.103	79.2		85.6		86.1		84.4		86.4		87.5	
0.0933	68.5	41	80.8	53	76.9	55.6						
0.0845	72.3	47	78.7	57.1	79.5	58.32						
0.0765	71.6	47.2	81.4	59.72	82.7	62.5						
0.0693	72.7	52.8	83.4	62.12	82.4	64.86						
0.0627	75.4	55	82.4	68.3	83.7	69.9						
0.0568	75.4	55.9	85	72.53	84.3	75.1						
0.0514	76.9	62.5	83.7	75.6	85.4	77.7	89	119.88	91.5	122.28	98	125.94
0.0465	77.2	64.4	84	76.1	86.3	78.7	87	124.65	90.5	130.17	96.8	132.48
0.0422	78.3	66.7	85.4	81.28	84.7	82.7	92.5	126.05	91.7	133.49	97.4	132.83
0.0382	79	65.5	86.5	83.5	85.8	84.2	88.3	131.23	93.2	138.43	97.6	137.2
0.0344	85	70.31	88.5	89	85.6	87.7	90	130.57	92.5	143.76	97.5	139.88
0.02878	83.7	71.22	86.5	93.8	87.1	94.6	93	133.74	94.2	142.57	99.6	141.34
0.02634	84.7	72.21	88.5	95.2	88.5	96.3	96.7	150.2	99.7	154.8	99.7	174.64
0.02431	85	72.93	89	101	89.5	99.7	96.4	168.63	98	180.61	98.1	182.2
0.0223	87.3	74.63	89	99.3	89.9	103.3	99.3	178.14	99.4	180.66	100.3	182.4
0.02062	87.6	75.88	90.5	103.4	91.4	106.8	98.8	188.97	100.2	206.86	99.7	192.47
0.01995	87.8	83.56	90.7	112.32	90.7	114.98	99.7	164.45	100.2	172.85	102	158.6
0.0173	85	82.30	90.1	116.8	90.5	117.66	100.5	168.54	101.5	179.12	101.6	166.84
0.01537	86.8	73.36	91	119.56	91.2	121	99.7	172.73	103.6	182.28	102.2	172.94
0.01334	87.8	73.36	90.6	126.95	91	128.43	100	176.76	104.6	187.1	102.2	179.5

As can be seen from the results in TABLE 2 and Fig. 1, the niobium-silicon wire had a much higher tensile strength and hardness than the niobium-zirconium wire at about 0.050 inches diameter and below.

Also, electrical leakage tests (40 volts at 90%) were conducted for wire (wire-anode assemblies in capacitor test conditions) or anodes with select silicon master blends (Experiments #1 and #2) and presented in Fig. 2. The tests were conducted for anode assemblies with lead wires made at various sintering temperatures. As can be seen from the results in TABLE 3 below and Fig. 2, the niobium-silicon wire is acceptable for use at sintering temperatures of 1250°C and above, but not lower, complying with the current tantalum capacitor grade wire specification leakage of 0.6 $\mu A/in^2$ at 1250°C.

TABLE 3

	(@1250°C) Leakage $\mu A/in^2$
niobium ingot	0.1
niobium-zirconium	0.25
Experiment #1	0.35
Experiment #2	0.6
Specification	0.6

Side and front views of examples of niobium-silicon capacitor lead wires of the present invention bonded to anode compacts are illustrated in Figs. 3A-3F. Figs. 3A and 3B illustrate a niobium-silicon capacitor lead wire 10 butt welded to an anode compact 12. Figs. 3C and 3D illustrate a niobium-silicon capacitor lead wire 10 imbedded for a length 14 within compact 12. Figs. 3E and 3F illustrated yet another attachment technique of welding the lead wire 10 to the top 16 of the compact 12. The lead wire 10 of any of Figs. 3A-3F and/or the compact 12 of any such figures can be circular or flat (ribbon form) or other shapes.

Also, electrical leakage tests (40 volts at 90%) were conducted for wire (wire-anode assemblies in capacitor test conditions) or anodes with select silicon master blends (Experiments #3,4 and 5) and presented in Fig. 4. The tests were conducted for anode assemblies with lead wires made at various sintering temperatures. As can be seen from the results in TABLE 4 below and Fig. 4, the niobium-silicon wire is acceptable for use at sintering temperatures of 1150°C and above, but not lower, complying with the current tantalum capacitor grade wire specification leakage of 0.6 $\mu A/in^2$ at 1150°C.

TABLE 4

	(@1150°C) Leakage $\mu A/in^2$
niobium ingot	0.1
niobium-zirconium	0.25
Experiment #3	0.09
Experiment #4	0.118
Experiment #5	0.103
Specification	0.6

Artifacts of electrolyte impregnation and pyrolysis cathode attachment and packaging all well known to those skilled in the art are omitted from the figures for convenience of illustration

Other embodiments of the present invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only.

In this specification, the following conversion factors may be used where non-metric measurements appear:

1 inch = 25.4mm

n°F = (n – 32)*5/9°C, where n is any number

WHAT IS CLAIMED IS:

1. A process for making a silicone-doped niobium lead wire comprising:

(a) forming a low oxygen niobium powder by hydriding a niobium ingot or a niobium bar and grinding or milling the ingot or the bar, and thereby making a powder having a Fisher Average Particle Diameter particle size range of less than 150 microns,

(b) dehyriding and deoxidizing the powder and forming a low oxygen niobium powder,

(c) blending the low oxygen niobium powder with a silicon additive powder and compacting the powder by cold isostatic pressing to a bar;

(d) thermomechanically processing the bar into a rod, and

(e) subjecting the rod to a combination of rolling and cold drawning steps, and forming a capacitor grade silicone-doped wire.

2. The process of Claim 1, wherein step b) includes deoxidating the powder.

3. The process of Claim 1, wherein the silicon is added in an amount that is less than 600 ppm.

4. The process of Claim 1, wherein the silicon is added in an amount ranging from 150 to 300 ppm.

5. The process of Claim 1, wherein the rod is subjected to a schedule of reductions and intermediate anneals involving annealing, rolling, annealing, reducing, and drawning steps.

6. The process of Claim 1, wherein the rod is subjected to a combination of steps comprising (i) a first annealing step, (ii) a rolling step, (iii) a second annealing step, (iv) a reducing step, and (v) a drawning step.

7. The process of Claim 6, wherein the schedule of reductions and intermediate anneals involve a combination of steps that involves: annealing at a temperature of 1371°C for 1.5 hours; rolling to a diameter of 11.18mm; annealing at a temperature of 1371°F for 1.5 hours; reducing to a diameter of 2.54mm diameter; drawning to a wire having a diameter of at least 0.127mm

8. The process of Claim 1, wherein the wire further contains metal component selected from the group consisting of tantalum, zirconium, titanium, and combinations thereof.

9. The process of Claim 1, wherein the niobium powder has an oxygen level that is below 400 ppm.

10. The process of Claim 1, wherein the wire has a tensile strength exceeding capacitor-grade niobium wire and niobium-zirconium alloys derived directly from ingot metallurgy.

11. A capacitor grade wire having a tensile strength exceeding capacitor-grade niobium wire and niobium-zirconium alloys derived directly from ingot metallurgy, wherein the wire is made from a process comprising:

(a) forming a low oxygen niobium powder by hydriding a niobium ingot or a niobium bar and grinding or milling the ingot or the bar, and thereby making a powder having a Fisher Average Particle Diameter particle size range of less than 150 microns,

(b) dehyriding the powder and forming a low oxygen niobium powder,

(c) blending the low oxygen niobium powder with a silicon additive powder and compacting the powder by cold isostatic pressing to a bar;

(d) thermomechanically processing the bar into a rod, and

(e) subjecting the rod to a combination of rolling and cold drawning steps, and forming the silicone-doped wire.

12. The capacitor grade wire of Claim 11, wherein step b) includes deoxidating the powder.

13. The capacitor grade wire of Claim 11, wherein the silicon is added in an amount that is less than 600 ppm.

14. The capacitor grade wire of Claim 11, wherein the silicon is added in an amount ranging from 150 to 300 ppm.

15. The capacitor grade wire of Claim 11, wherein the rod is subjected to a schedule of reductions and intermediate anneals involving annealing, rolling, annealing, reducing, and drawning steps.

16. The capacitor grade wire of Claim 11, wherein the rod is subjected to a combination of steps comprising (i) a first annealing step, (ii) a rolling step, (iii) a second annealing step, (iv) a reducing step, and (v) a drawning step.

17. The capacitor grade wire of Claim 16, wherein the schedule of reductions and intermediate anneals involve a combination of steps that involves: (i) annealing at a temperature of 1371°C for 1.5 hours; rolling to a diameter of 11.18mm; annealing at a temperature of 1371°C for 1.5 hours; reducing to a diameter of 2.54mm diameter; drawning to a wire having a diameter of at least 0.127mm.

18. The capacitor grade wire of Claim 11, wherein the wire further contains a metal component selected from the group consisting of tantalum, zirconium, titanium, and combinations thereof.

19. The capacitor grade wire of Claim 11, wherein the niobium powder has an oxygen level that is below 400 ppm.

20. The capacitor grade wire of Claim 11, wherein the wire has a tensile strength exceeding capacitor-grade niobium wire and niobium-zirconium alloys derived directly from ingot metallurgy.

21. A process for making a silicone-doped niobium lead wire, substantially as herein described with reference to Figures 1 to 4 of the accompanying drawings and tables 1 to 4 of the specification.

22. A capacitor grade wire substantially as herein described with reference to Figures 1 to 4 of the accompanying drawings and tables 1 to 4 of the specification.

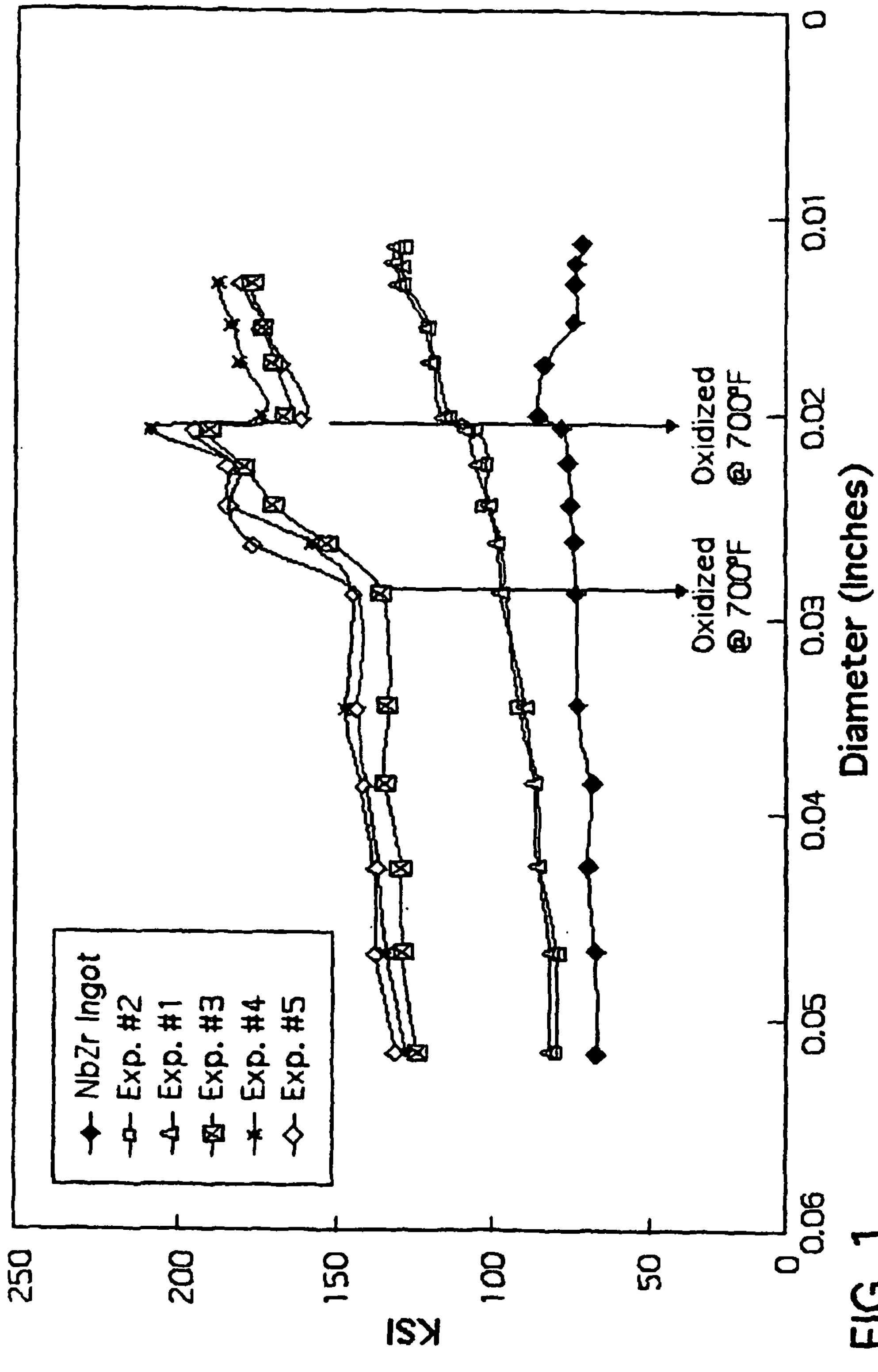
NbZr Ingot
Exp. #2
Exp. #1
Exp. #3
Exp. #4
Exp. #5
Oxidized @ 700°F
Oxidized @ 700°F
KSI
250
200
150
100
50
0
0.06
0.05
0.04
0.03
0.02
0.01
0
Diameter (Inches)

FIG. 1

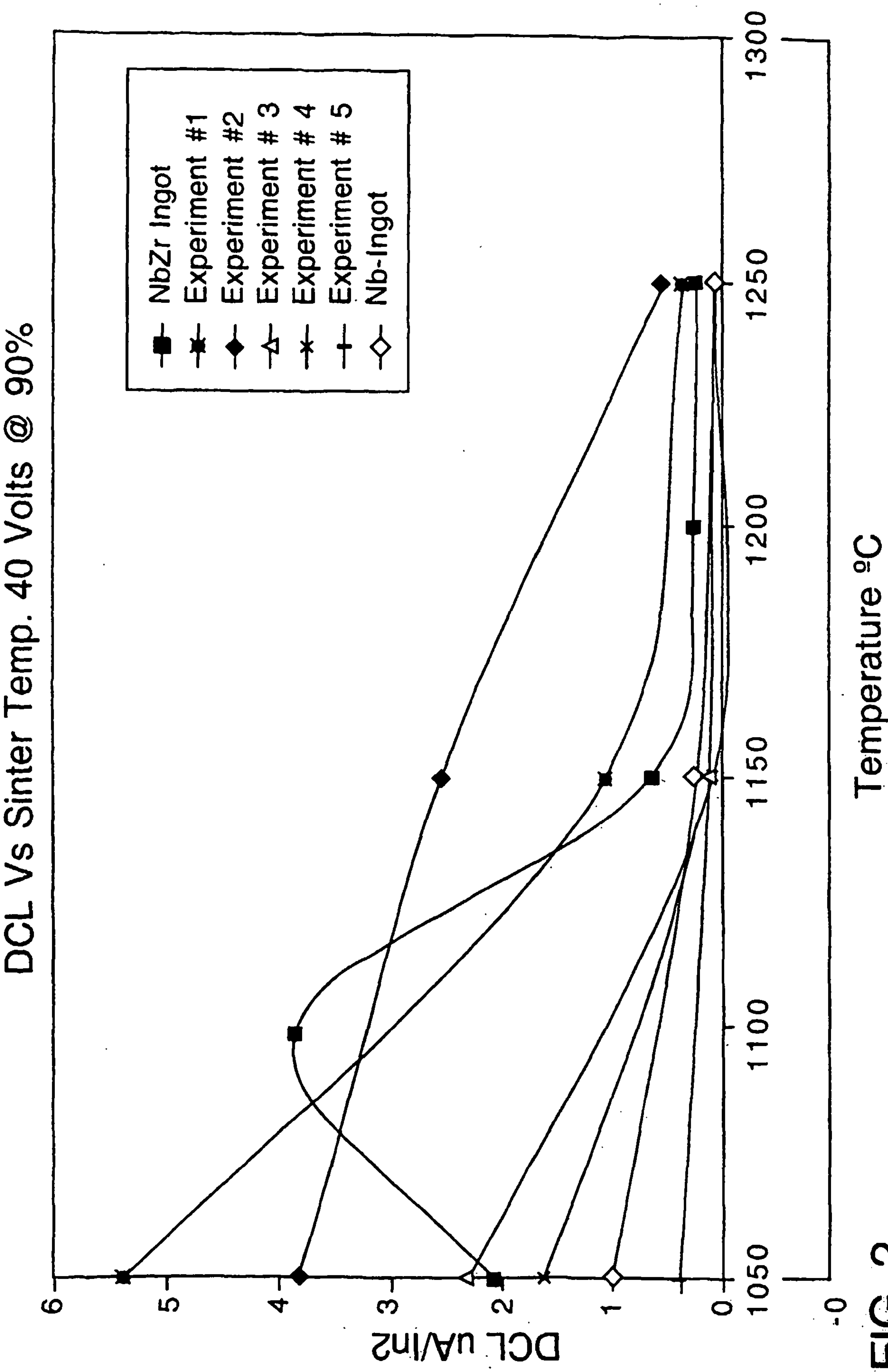
DCL Vs Sinter Temp. 40 Volts @ 90%
NbZr Ingot
Experiment #1
Experiment #2
Experiment # 3
Experiment # 4
Experiment # 5
Nb-Ingot
DCL uA/in2
6
5
4
3
2
1
0
-0
1050
1100
1150
1200
1250
1300
Temperature ºC

FIG. 2

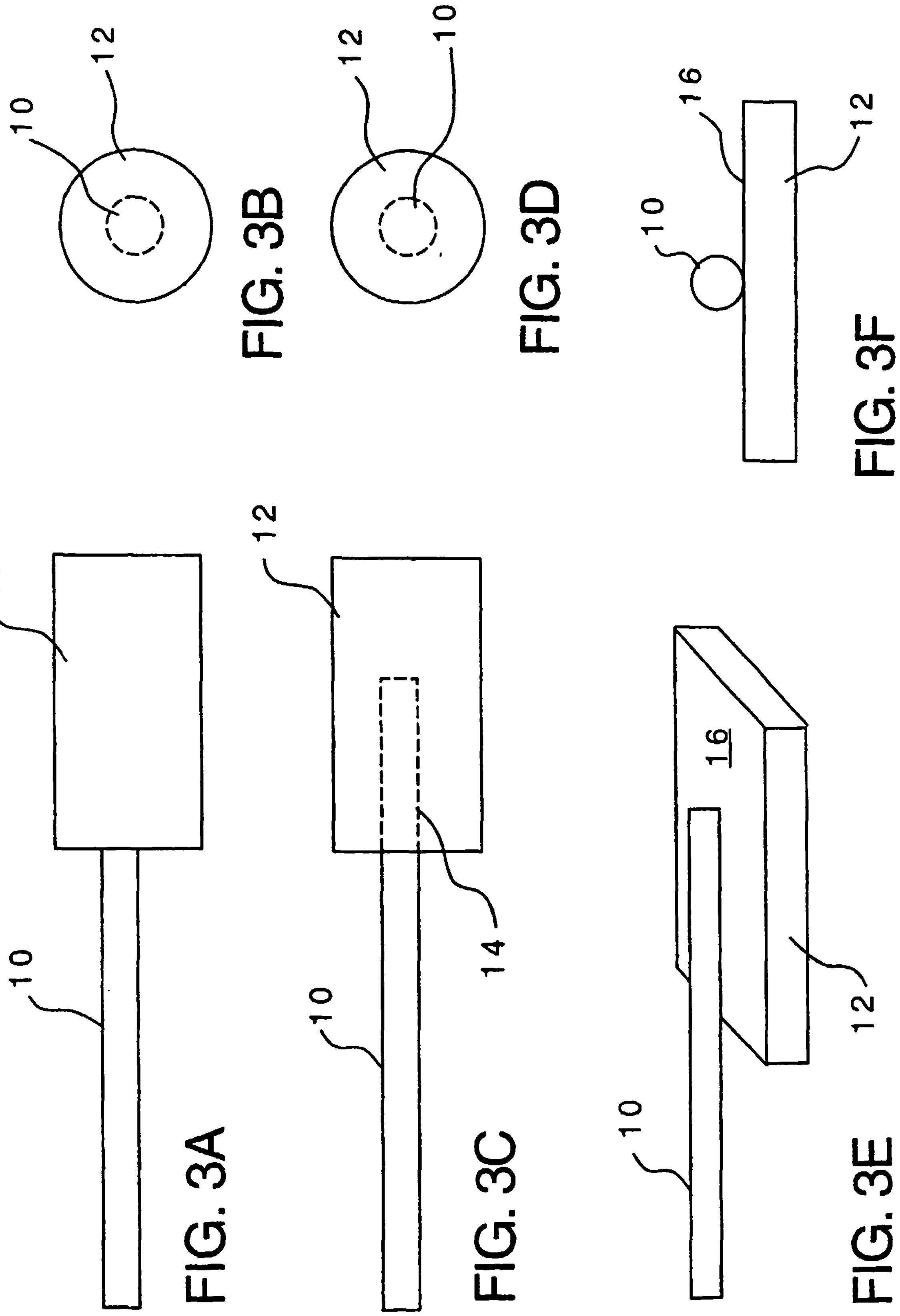

FIG. 3A FIG. 3B FIG. 3C FIG. 3D FIG. 3E FIG. 3F

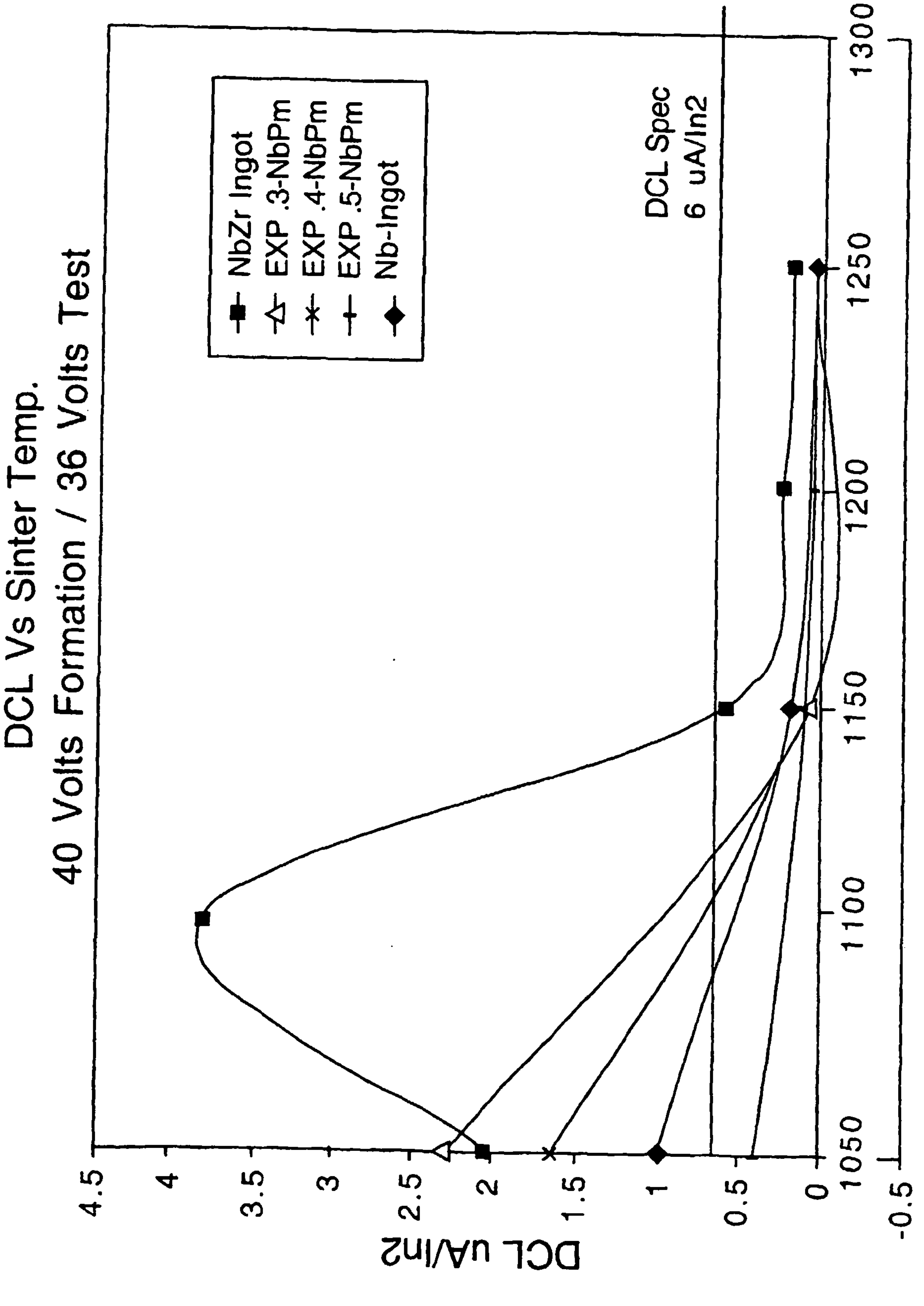
DCL Vs Sinter Temp.
40 Volts Formation / 36 Volts Test
NbZr Ingot
EXP .3-NbPm
EXP .4-NbPm
EXP .5-NbPm
Nb-Ingot
DCL Spec
6 uA/In2
DCL uA/In2
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
1050
1100
1150
1200
1250
1300
Temperature ºC

FIG. 4