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A Review of the Extractive Metallurgy of Niobium [1]

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[1] This work was done in part under contract AEC-AT(30-1)-1894 sponsored by the Division of Research, U.S. Atomic Energy Commission.

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ABSTRACT

The preparation of niobium has been attempted by a number of chemical and electrochemical routes. Chemical reduction of oxides and halides such as Nb_2O_5, K_2NbOF_5, K_2NbF_7, and $NbCl_5$ has been conducted with varying degrees of success. Aqueous electrochemical reduction has not yet yielded a metallic deposit. The electrolysis of molten baths containing K_2NbOF_5 or K_2NbF_7 has produced niobium metal.

The more promising methods of preparation for Nb metal at the present time include the reaction of Nb_2O_5 with C, the H_2 and active metal reduction of $NbCl_5$ and electrolysis of K_2NbF_7-NaCl melts.

A Review of the Extractive Metallurgy of Niobium

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Introduction

The metal niobium (columbium) was first isolated in 1907, but has been produced commercially only since about 1930, and only in very minor amounts. Several interdependent factors account for this, including lack of known uses for the metal, high cost of ores and product metal, difficulties in separation of ores, and lack of knowledge concerning the chemistry of niobium.

The only uses for the metal thus far developed are in the electronic industry and as an alloying agent in the form of ferroniobium. However, in recent months, interest in the metal has shown a marked increase due in particular to properties of the metal which indicate a potential value in the field of atomic energy. Among the properties of interest are its low neutron cross section, refractory nature, corrosion resistance, superconductivity, and its low work hardening nature. A summary of basic properties of the metal are listed in Table I.

This summary of the known properties of the metal quickly indicates why interest has been revived in niobium metallurgy. The need for new structural materials is

Table I

Properties of Niobium (1-5)

Melting Point	2468 ± 10°C
Boiling Point	ca. 3300°C
Specific Heat (cal/g. atom/°C)	6.012
Density (g/cc)	8.66
Lattice Type (no phase transformations)	BCC
Lattice Constant (291°K)	3.3004
Coefficient of Linear Expansion/°C	7.1 x 10^{-6}
Atomic Volume (cc/g atom)	10.83
Heat of Sublimation (Kcal/g atom)	170.9
Electrical Resistivity (μ ohm cm -0°C)	15.22
Temp. Coeff. of Elect. Resistivity °C	0.00395
Electron Work Function (ev)	4.01
Ionization Potential	6.77
Positive Ion Emission (ev)	5.5
Neutron Cross Section (barns-abs)	1.1 ± 0.1
Electrochemical Eq. (+5) g/A hr.	0.6932
Magnetic Susceptibility (CGS)	2.28 x 10^{-6}
Tensile Strength, Annealed Sheet (psi)	44-50,000
" " , Cold Worked " "	100,000
Shear Modulus (dynes/cm^2)	3.75 x 10^{-11}
Young's Modulus (dynes/cm^2)	10.4 x 10^{-11}
Poissons Ratio	0.38
Reaction with oxygen (7.6 cm O_2 pres.)	parabolic to 375°C
" " nitrogen	Same as O_2 at 375°C (parabolic)
" " hydrogen	Starts at 250°C
Price per lb. (1957)	ca. $120.00

continually increasing in the areas of reactor technology and nuclear propulsion and a material with neutron cross section, mechanical and stress rupture properties exhibited by niobium cannot be overlooked.

Niobium possesses an outstanding potential as a material of construction in aircraft gas turbine engines. Preliminary data on some Nb base alloys indicate that they can be used at temperatures considerably in excess of the present 1800°F. This would enable higher power/weight ratios to be achieved.

Niobium was first discovered in 1801 (1,6) when Hatchett noted an unfamiliar substance in a Connecticut ore. He named the material columbium after its source. In 1802 Ekeberg noted an acidic oxide of an element which he called tantalum. About 40 years later, H. Rose showed that some columbites contained two acidic oxides, tantalum, and another which he called niobium. The latter was soon shown to be identical with columbium.

Elemental niobium was first prepared by Von Bolton (7) in 1907 at Siemens-Halske through a sodium reduction of the fluoniobate.

Balke (6)7,8) developed the first commercial method in 1929. The process was analogous to that for tantalum and involved a fusion electrolysis of K_2NbF_7 or K_2NbOF_5 with or without addition of Nb_2O_5 and alkali chlorides or fluorides.

Since that time a variety of other procedures have been developed or proposed for preparation of niobium although none of these have been applied to commercial practice.

It is the purpose of this paper to review the approaches made to the extractive metallurgy of niobium and to demonstrate which approaches offer the most promise.

Niobium is similar in many respects to titanium, zirconium, vanadium and tantalum and to a lesser extent, to all the multivalent transition metals. This being the case, it would be expected that analogous methods of preparation would apply to niobium as are used for zirconium, tantalum, etc.

The broad areas of approach that have been investigated for niobium are the following:

(1) Reduction of oxides

(2) Reduction of halides and oxyhalides.

Each of these may in turn be broken down into 3 categories; (a) active metal reduction, (b) non-metal reduction, and (c) electrolytic reductions. Each of these six process types is considered and the previous work briefly reviewed. Free energy considerations have been estimated for most of the reaction types in order to give some relative idea as to the value of and justification for each approach.

Reduction of Oxides

Niobium forms at least three oxides, Nb_2O_5, NbO_2, NbO, and possibly Nb_2O_3. The pentoxide is probably the most readily available form of the element and thus is an attractive starting material. The other oxides are also easily prepared by simple reductions, e.g., by hydrogen.

Thermodynamic data on 3 oxides as reported by Glassner (9) is shown in Figure 1. It is seen that the oxides are quite stable and would probably be reduced only by the active metals.

Active Metal Reductions

Using the data in Figure 1 together with data from Quill (10), free energy calculations were made for reductions using sodium, magnesium, calcium, and aluminum as representative reductants. The results shown in Figures 2, 3, 4 and 5 indicate that reductions of niobium oxides using magnesium, calcium and aluminum are thermodynamically feasible, but the sodium reaction is not. Presumably similar curves would be obtained for other alkali and alkaline earth metals as for sodium and calcium respectively.

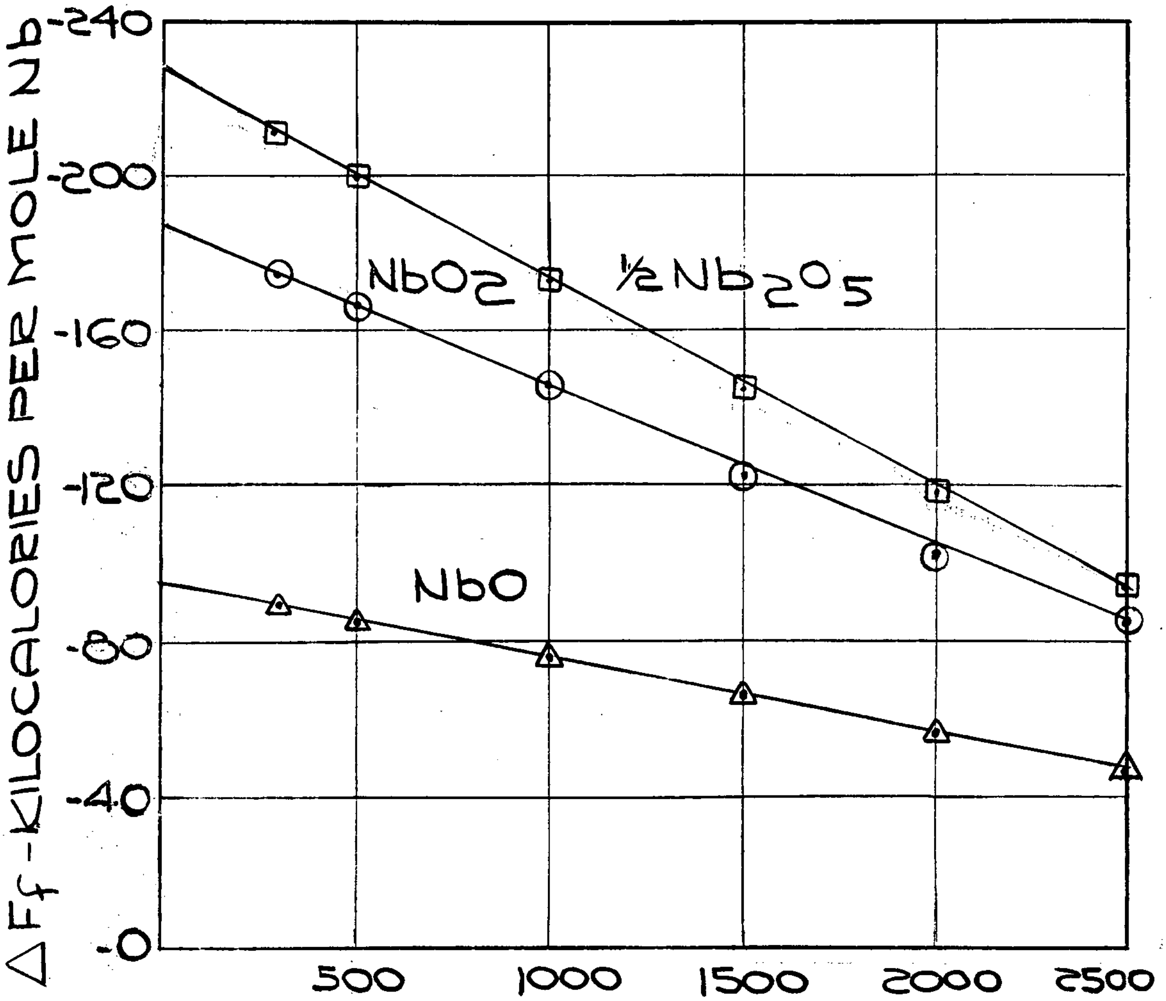


FIG. 1

FREE ENERGY OF FORMATION OF NIOBIUM OXIDES ACCORDING TO GLASSNER, ANL-5107, AUGUST, 1953

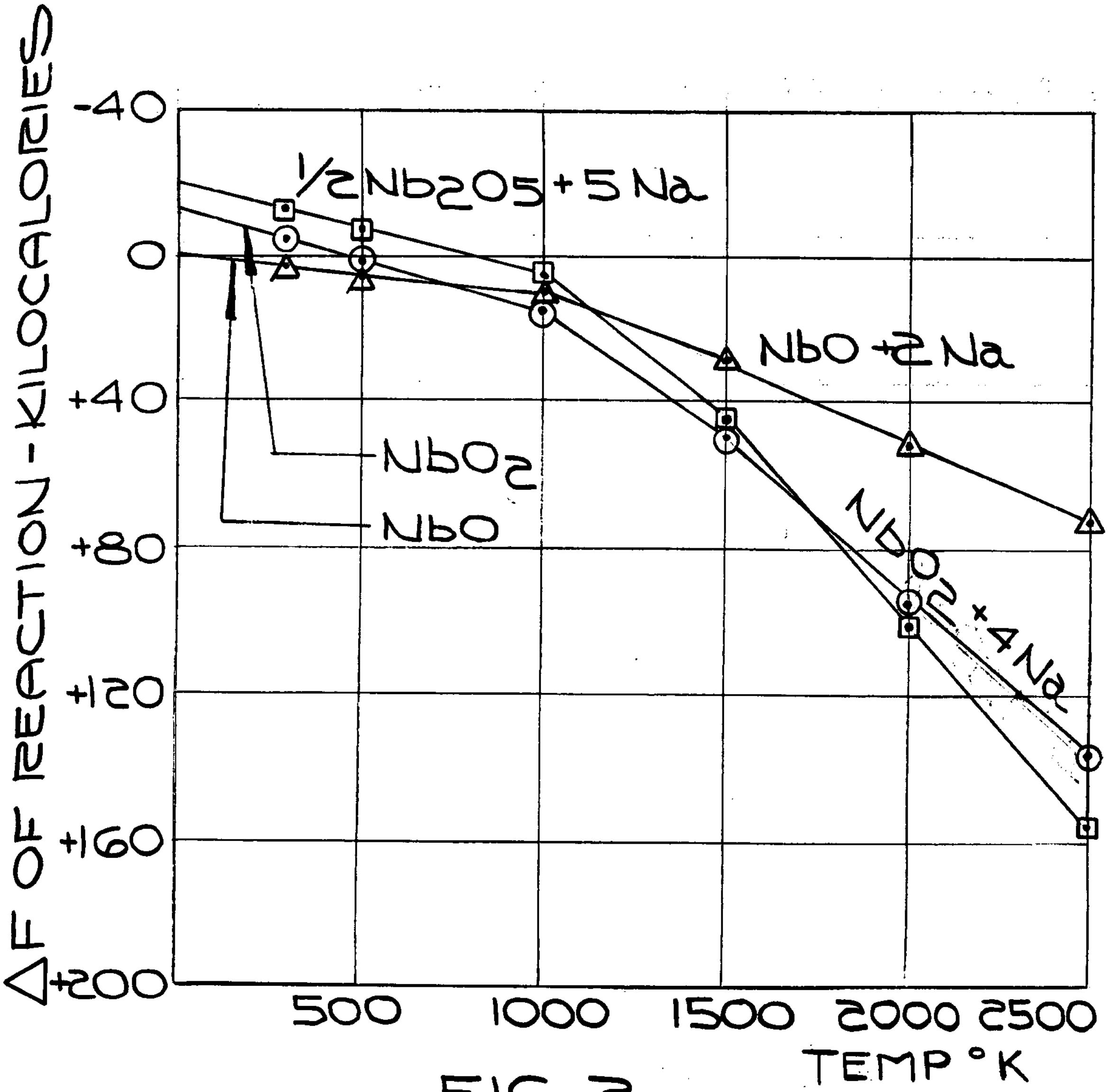


FIG. 2
SODIUM REDUCTION OF OXIDES

(Values over 1153°K not corrected for vapor phase of Na)

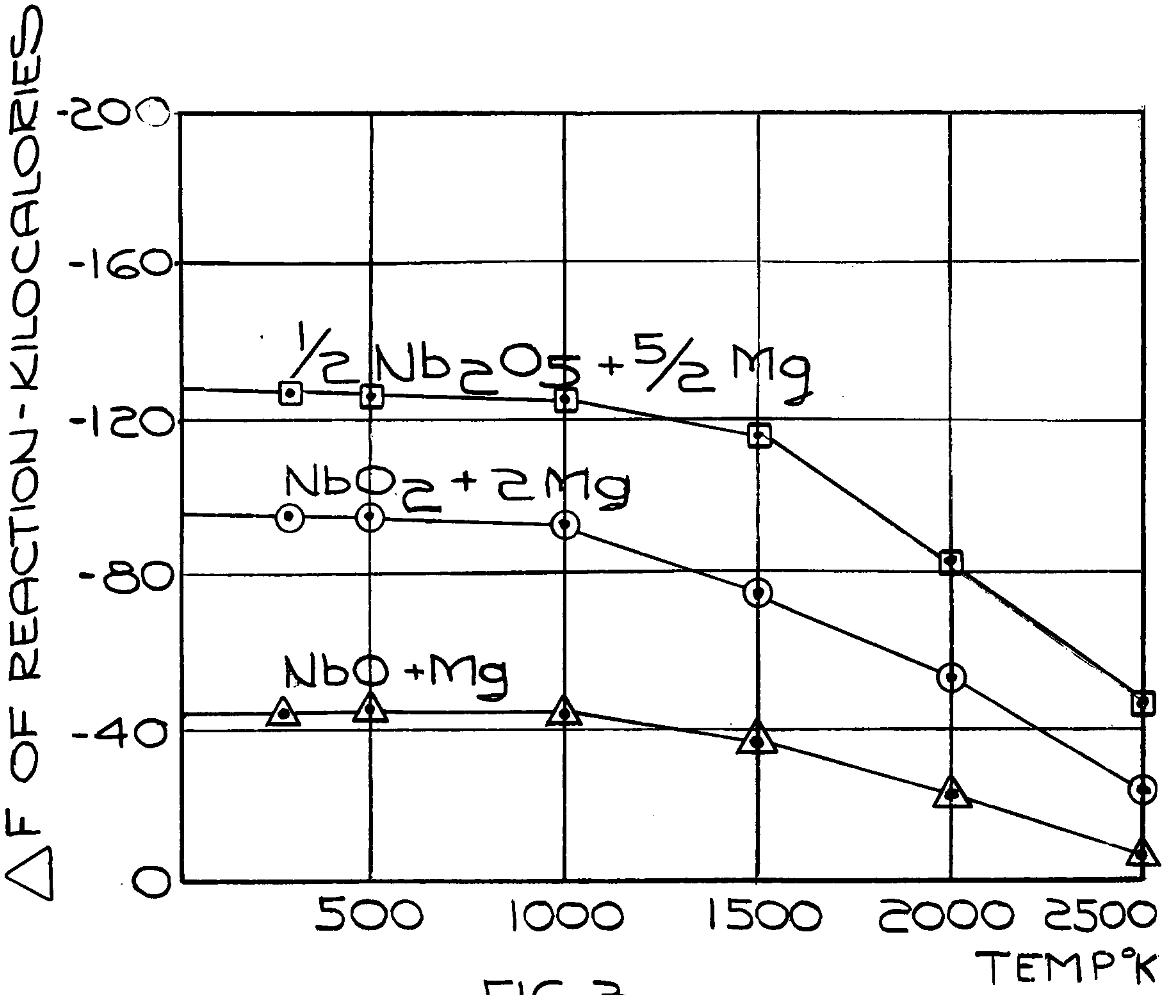


FIG. 3

MAGNESIUM REDUCTION OF OXIDES

(Values over 1380 °K not corrected for vapor phase of Mg)

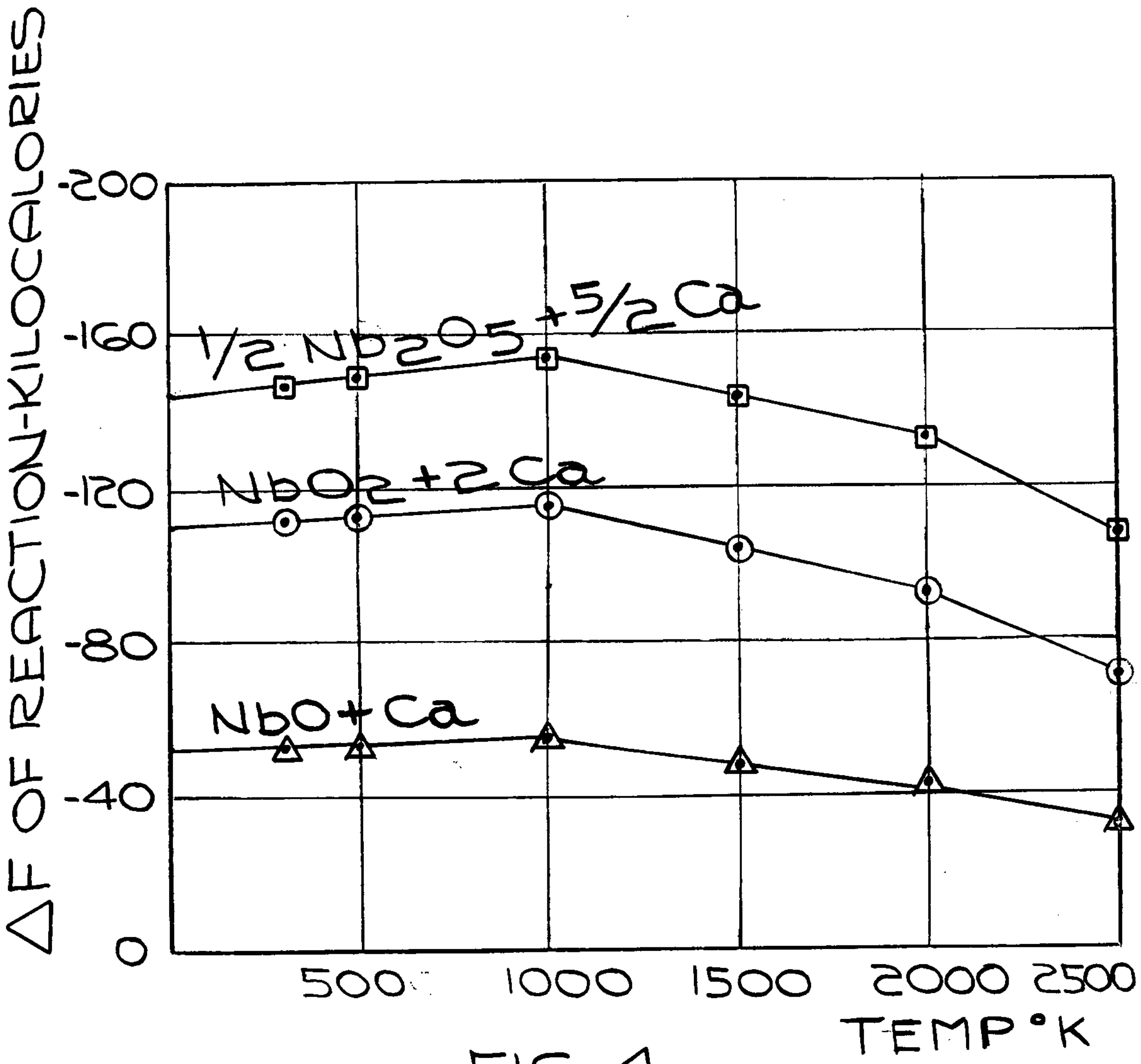


FIG. 4
CALCIUM REDUCTION OF OXIDES

(Values over 1513 °K not corrected for vapor phase of Ca)

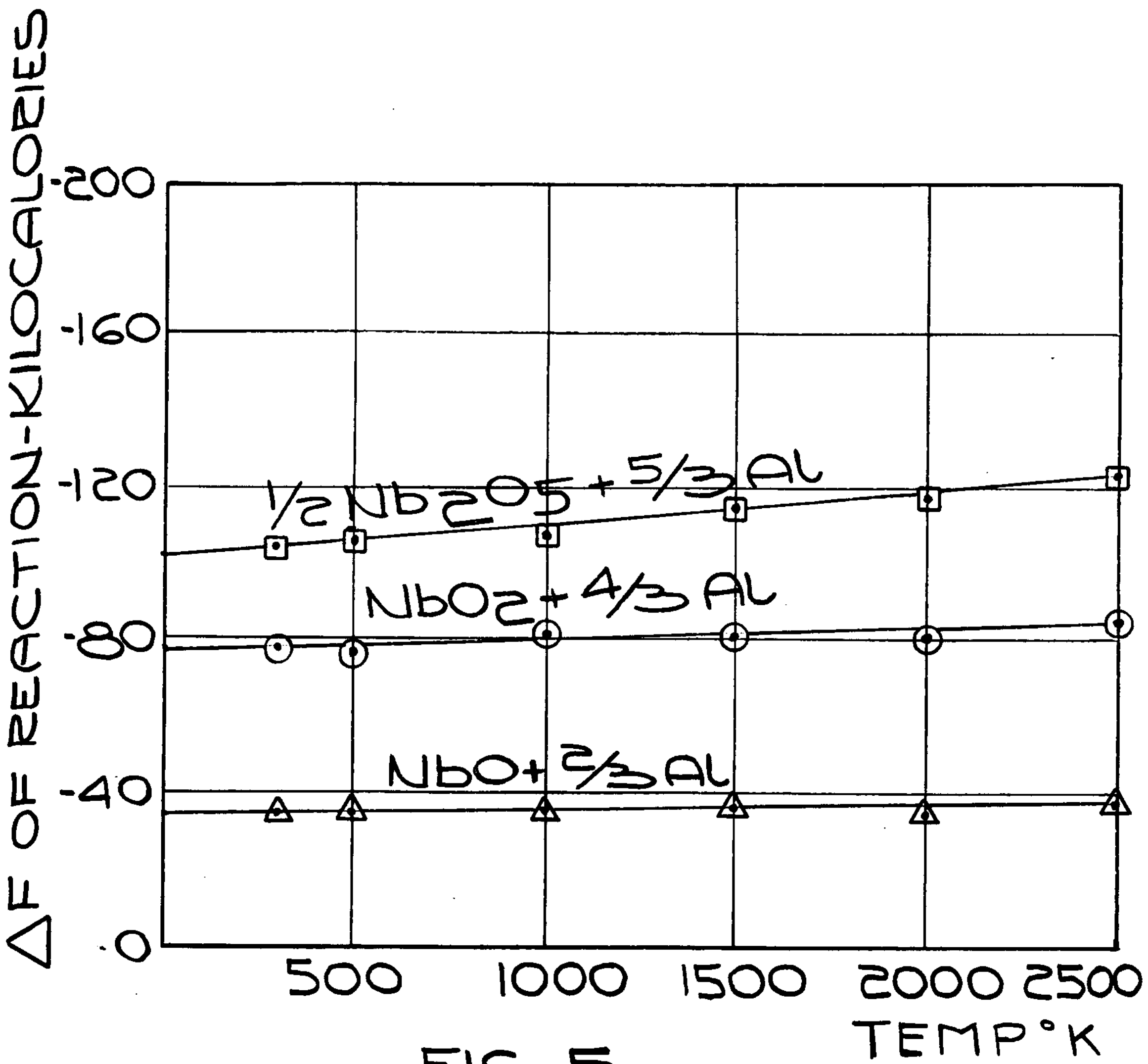


FIG. 5

ALUMINUM REDUCTION OF OXIDES

Both magnesium and sodium reductions become less favorable as the temperature is raised, but aluminum reduction is slightly favored with increasing temperature. This would indicate that the aluminothermic or thermit type of reaction might offer some promise for niobium.

Even though the Mg and Al reductions of the oxides are favorable, such reactions are not a particularly desirable approach to niobium preparation. In all such cases, a major separation problem would exist for the insoluble by-product oxides such as MgO or Al_2O_3. In addition, the solubility of Al in Nb as well as compound formation between these two metals makes a good separation extremely difficult.

As might be predicted from the free energy of reaction curves, practically all reported work in this area has concerned reduction of the pentoxide with alkaline earths or aluminum. There is no report of a ductile niobium product being prepared by such a reduction despite the favorable free energy relations. However, it must be noted that the previous ΔF values are only approximate and do not consider alloying or solution energies.

The work of several investigators in this area is listed in Table II. In several of the experiments, Nb alloys have been prepared. Particularly in the case of

Table II

Metallic Reduction of Oxides

System	Reference	Conditions	Results
Nb_2O_5	Bridge(1922)(11)	high temp.	Nb metal
	Leemans(1939)(12)	w. Ta_2O_5	Nb-Ta slag
Nb_2O_5-Ca	Bridge(1922)(11)		Nb metal
	Marden(1927)(13)	$CaCl_2$ melt + alk metal (v)-bomb-900°	Nb metal powder
	Leemans(1939)(12)	w. Ta_2O_5	Nb-Ta slag
	Dickson(1956)(14)	proposed method	--
Nb_2O_5-Al	Pennington(1896)(15)	K_3AlF_6-NaCl melt	Nb-Al alloy
	Goldschmidt(1898)(16)	thermit reaction	Alloy
	Bridge(1922)(11)		Nb metal
	Leemans(1939)(12)	w. Ta_2O_5	Nb-Ta slag
Nb_2O_5-Misch-Metal	Weiss(1904)(17)		Nb-Al alloy
	Muthman(1907)(18)		Nb-Al alloy
Nb_2O_5-CaC_2	Leemans(1939)(19)	elec. furnace	Nb-Ta alloy
Nb_2O_5-Ca, Mg, Li, Ba, or Al Silicide + Ca or Ba hydride	Gardner(1950)(20)	react in current of air	$NbSi_2$; Si distilled at 3300°
Nb_2O_5-S or CS_2-CaH_2 or BaH_2	Gardner(1951)(21)	2 steps; NbS_2(1), Nb(2)	pure Nb

Al-Nb, it has been reported that the separation is extremely difficult.

This approach does offer one promising potential in that it might be employed as a means of preparing a crude Nb product to be employed as a base material for a subsequent refining process.

Non-Metal Reductions

The most commonly used non-metallic reductants are hydrogen and carbon. Free energy considerations for their reduction of Nb oxides are shown in Figures 6 and 7. All of the curves are for reduction to metal except the two H_2 reductions for Nb_2O_5 in Figure 6.

It is seen that the carbon reduction is favorable at about 1500°K and above. The hydrogen reaction does not become favorable until over 3000°K. Thus assuming proper equilibria and kinetic considerations, the carbon reduction of the oxide would be an attractive approach. The hydrogen reduction is seen to be considerably more attractive for partial reduction of Nb_2O_5.

It is seen from Figure 6 that Nb_2O_5 is readily hydrogen reduced to NbO_2. The same applies to Nb_2O_3, but reduction to NbO is difficult and proceeds only above 2000°C even in

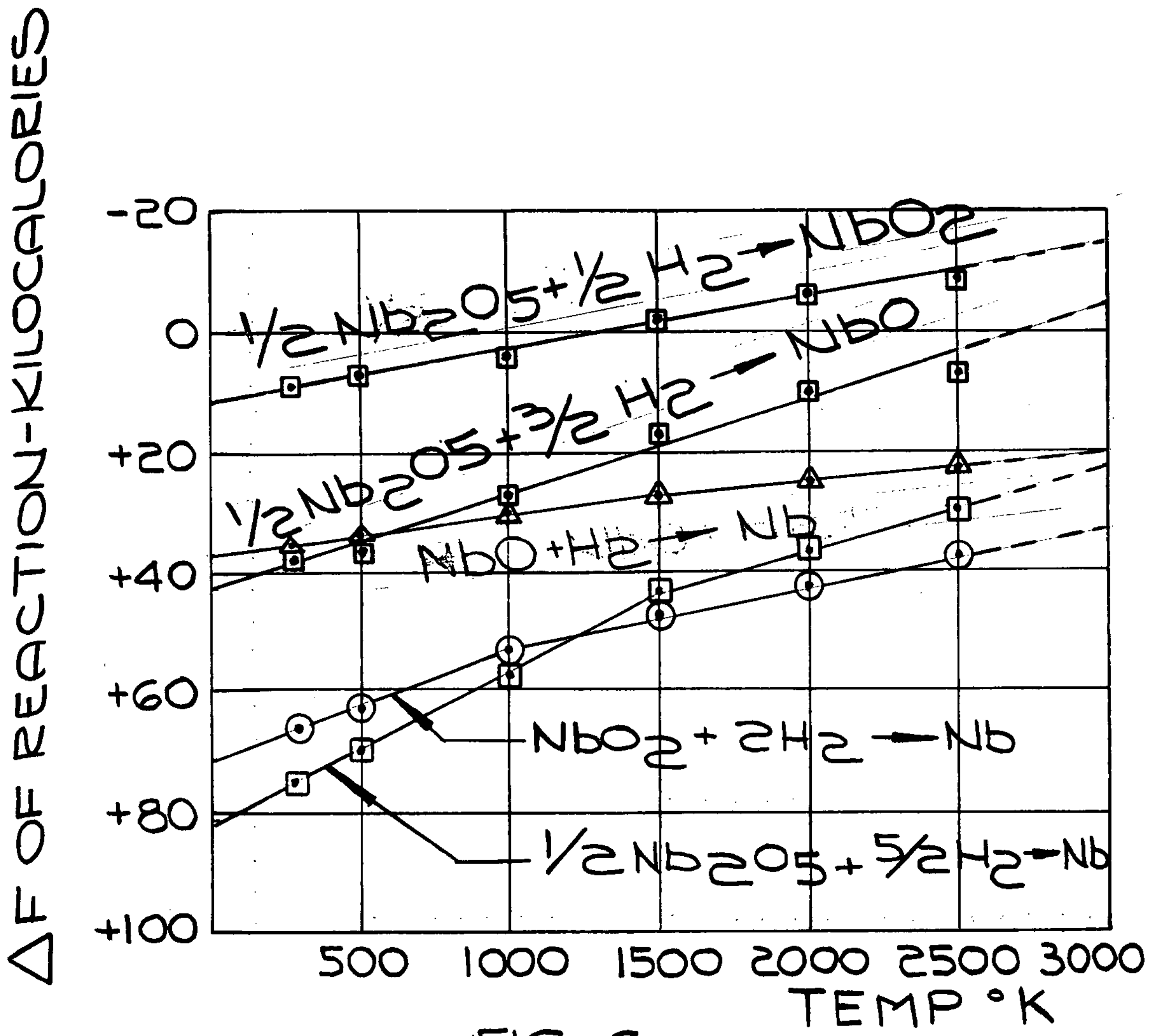


FIG. 6
HYDROGEN REDUCTION OF OXIDES

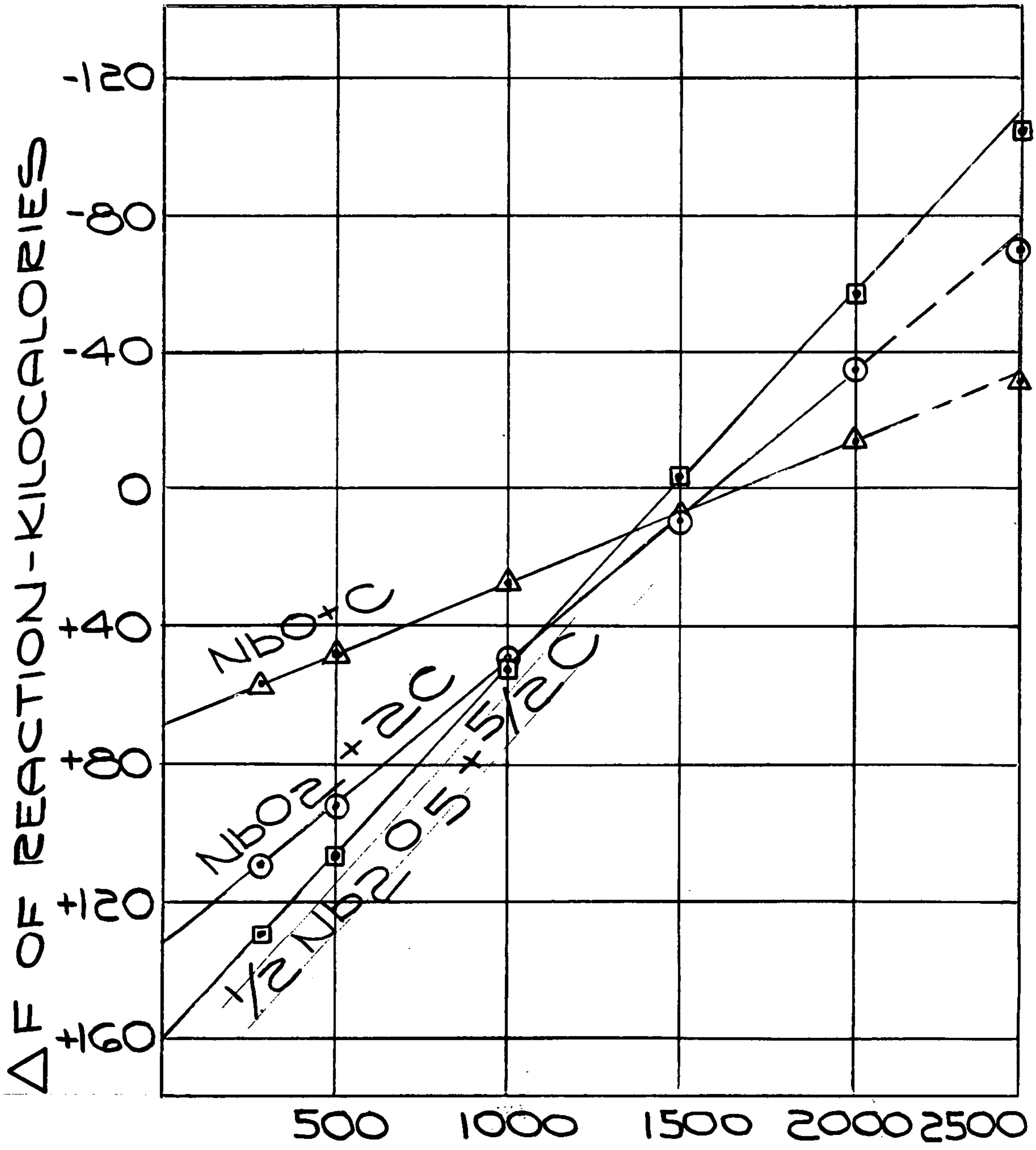


FIG. 7

CARBON REDUCTION OF OXIDES

a high vacuum. Generally, there would be no great advantage in obtaining the lower oxide unless it could be used in a secondary step where Nb_2O_5 could not, e.g., in an electrolytic process.

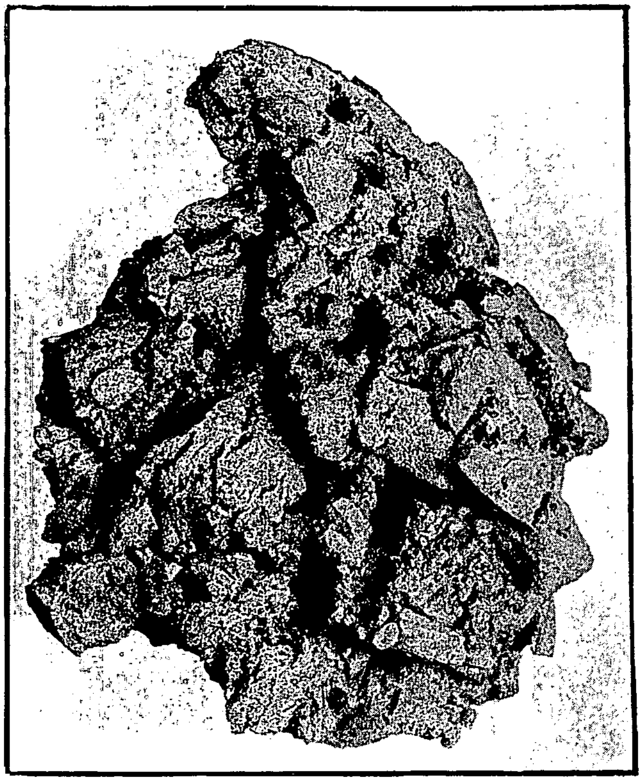
Figure 8 is a sample of carbon reduced Nb_2O_5 containing over 99% metal.

Investigation in the area of non-metallic reduction has followed in general what would be predicted on the basis of thermodynamic considerations. A number of such investigations dealing with hydrogen, carbon and other non-metal reductants for Nb_2O_5 are listed in Table III. The NbC reduction of the oxide is a commercially used process.

Except for the preparation of filaments, there is no verified claim of a successful hydrogen reduction. Von Bichowsky (30) has claimed the preparation of Nb by a novel H_2 reduction wherein a mixture of Nb_2O_5 and an oxygen bearing Ni compound ($NiCO_3$, $NiCl_2 \cdot xH_2O$, etc.) is reduced yielding an Nb-Ni alloy. The Ni is then removed by a CO treatment.

There are a large number of reports of successful carbon reductions of Nb_2O_5, but in light of recent work, the purity of products so produced is in doubt.

Zintl (37) has reported a successful reduction using Si



Neg. 3239

Figure 8

Carbon reduced Nb_2O_5

Table III

Non-Metallic Reduction of Oxides

System	Reference	Conditions	Results
Nb_2O_5-H_2	Heany(1907)(22)		Nb filaments
	Kuzel(1912)(23)	white heat	Nb filament
	Dobkèvitch(1913)(24)	NH_3 in atmosphere	NbN filament
	Wartenberg(1923)(25)		claim Nb
	Rohn(1933)(26)	oxide on (1) metal bath-e.g. Fe	Nb filaments Nb alloys
	Grube(1939)(27)		NbO_2, Nb_2O_3, NbO, Nb_2O
	Kubaschewsky(1940)(28)		reduced oxides
	Brauer(1941)(29)		reduced oxides
	Von Bichowsky(1956)(30)	mixed w. Ni-O compd and reduced	Nb-Ni; Ni removed by CO
Nb_2O_5-C	St.Claire Deville (1868)(31)	Na_2CO_3 flux	carbonitride
	Moissan(1901)(32)		Nb + 2.3-3.4% C
	Von Bolton(1907)(57)	C reduced to NbO_2; NbO_2 heated in vac.	pure Nb ?
	Rohn(1934)(33)	NbC used	Nb metal
	Sue(1939)(34)		Nb_2O_4
	Balke(1940)(35)	NbC instead C at 1600-1800°C	pure Nb
Nb_2O_5-CO	Sue(1939)(34)		Nb_2O_4
Nb_2O_5 + any 2 of Fe, Fe_3C, CaC_2, C	Leemans(1938)(36)		
Nb_2O_5-Si or $NbSi_2$	Zintl(1942)(37)	1800°C vac.	pure Nb + SiO

or $NbSi_2$ as the reductant. This has not been confirmed.

Electrolytic Reduction

A logical use of the oxide in niobium extractive metallurgy was its use in a fused salt electrolyte, particularly in procedures analogous to the Hall process for Al, the Fansteel Ta process employing Ta_2O_5 in K_2TaF_7 plus other common chlorides.

It is extremely doubtful that there is any hope for obtaining niobium electrolytically in processes using aqueous or organic oxygen bearing electrolytes. Some work has been done but with no reported success. The behavior of Nb in this respect is very similar to that of Ti and Zr.

Fused salt methods employing oxides as a feed material are not considered promising because Nb forms stable Nb-O ions in such melts, and the possibilities of achieving pure metal from such systems is remote.

This is borne out by the literature. Several systems are summarized in Table IV, none of which produced a pure product. Relatively little work has been done on electrolysis of Nb oxides. Most of the reported procedures deal with aqueous electrolytes and have yielded either no cathodic product or a reduced oxidic material. The only confirmed

Table IV

Electrolysis of Oxides

Oxide	Reference	Electrolyte	Conditions	Results
Nb_2O_5	Peirce(1931)(38)	conc. NaOH		no deposit
	Driggs(1931)(39,40)	K_2NbF_7, Nb_2O_5	w/wo alk.halides	Nb metal
	Isgarishew(1933)(41)	40% KOH, $(COOH)_2$, citric acid		no deposit
	Golibersuch(1949)(42)	75% H_2SO_4	5-10°C-1.7 A/dm^2	non-metallic deposits, e.g. $K_8Nb_6(OH)_6(SO_4)_{12}$
	Hartman(1951)(43)	phosphate melts		NbP + phosphates
$Nb(OH)_5$	Koizumi(1944)(44)	oxalic or salicylic acid + 5% NH_4Cl	10 $Amps/dm^2$ Pt anode	Nb deposit on W, Mo or Ni
	Krylov(1955)(45)	H_2SO_4 + gelatin	polarographic study	2 stage reduction

successful procedure in the oxide electrolysis field is that of Driggs (39,40). This is not strictly an oxide procedure, employing a K_2NbF_7 diluent electrolyte. Recent work at this laboratory has shown this procedure incapable of producing a ductile pure product.

Hartman's work (43) using Nb_2O_5 in phosphate melts is of interest in that NbP was produced at the cathode. Such a material might be useful in a secondary process.

Theoretical decomposition voltages for the three common Nb oxides have been calculated as shown in Figure 9. Obviously any diluent electrolyte used must have an E value greater than that of the source electrolyte. All common alkali and alkaline earth halides satisfy this requirement.

Since the oxides are high melting, an electrolyte mixture would have to be used. This brings up the further problem of oxide solubility. In general, the Nb oxides are either insoluble or only slightly soluble in common chloride melts. They are soluble in fluorides such as the melt used by Driggs (39).

Reduction of Halides and Oxyhalides

Niobium forms halides in the +2, +3, +4 and +5 states. Of these only the fluorides and chlorides and their complexes

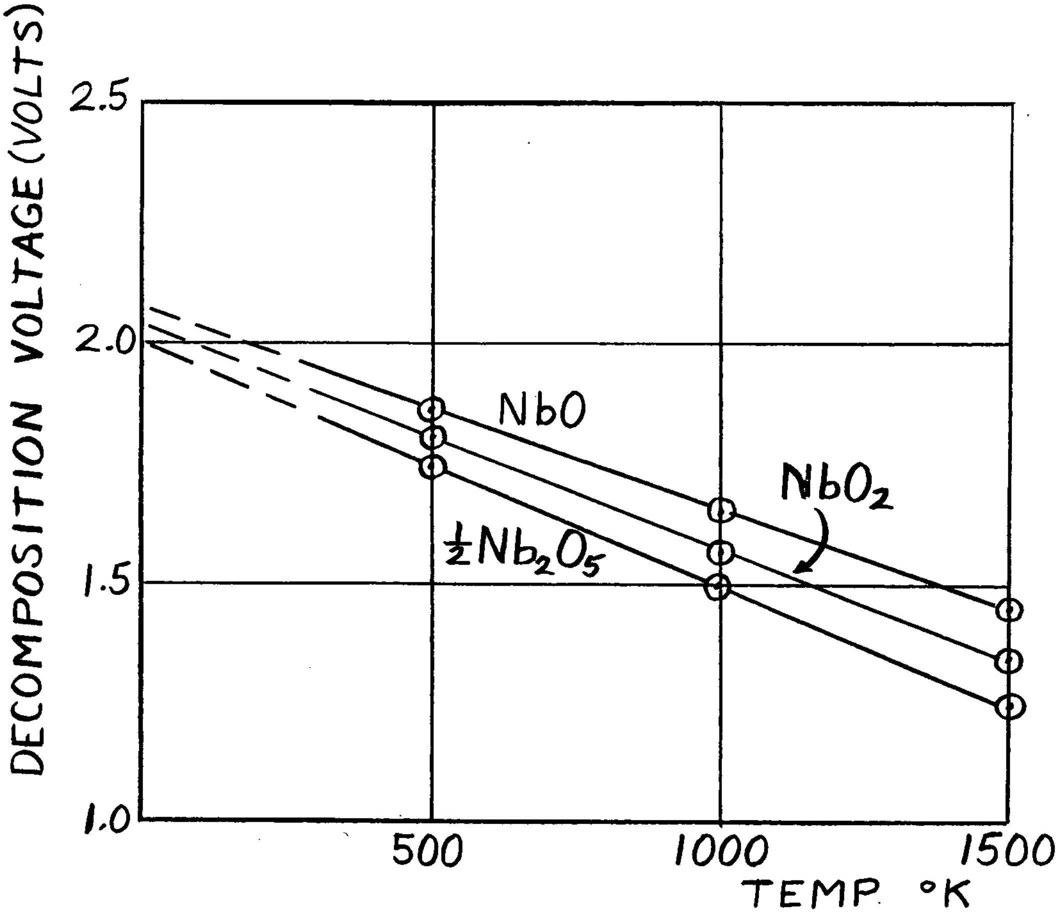


FIG ~~8~~ 9

THEORETICAL DECOMPOSITION VOLTAGES OF NIOBIUM OXIDES are of any present commercial importance. Of the fluorides only NbF_5 is known. This material also complexes with alkali and alkaline earth fluorides to give a variety of double fluorides of which the only commonly known species are K_2NbF_7 and the oxyfluoride complex, K_2NbOF_5. This latter material was the form in which Nb was recovered in the original Nb-Ta ore separation procedure (8).

The chlorides $NbCl_5$ and $NbCl_3$ are well known, but the tetrachloride and dichloride have not been extensively studied.

Halides which have been used as starting materials include only $NbCl_5$, K_2NbF_7 and K_2NbOF_5, although this discussion will also consider NbF_5 and $NbCl_3$ to some extent.

Free energy data is not available for the halides of Nb, but Brewer et al does give approximate values for VF_5, TaF_5, $TaCl_5$, VCl_4, $TaCl_4$, VCl_3, $TaCl_3$, VCl_2 and $TaCl_2$ up to 500 or 1000 °K. Values for NbF_5 have been estimated on this basis. The value for $NbCl_5$ and $NbCl_3$ has been estimated on the basis of Brewer's $TaCl_5$ data and data from McIntosh et al (47). Values for $NbCl_4$ and $NbCl_2$ are estimated from Brewer's data. McIntosh et al give the Kp value for the reduction of $NbCl_5$ to $NbCl_3$ as 1.98 at 500 °C. Thus $\Delta F_f(NbCl_5) - \Delta F_f(NbCl_3) \approx$ -46 Kcal. Since $NbCl_3$ is reduced by H_2 at 650 °C to Nb, its

ΔF_f at 650°C must be about -71 Kcal. Placing this value on a line parallel to curves for VCl_3 and $TaCl_3$ (Figure 12) gives a value of -78 Kcal at 500°C. Using the difference figure (-46 Kcal) means that $NbCl_5$ must have a ΔF_f of -124 Kcal at 500°C. It is also known that $NbCl_5$ disproportionates appreciably at 650°C so its ΔF_f value must be -115 Kcal or less. These two values were then used to locate the $NbCl_5$ curve shown in Figure 11. Figure 10 gives estimated values for NbF_5. Figure 12 gives the curve for $NbCl_3$ and Figure 11 for $NbCl_2$ and $NbCl_5$. The estimated values for $NbCl_3$ and $NbCl_5$ check well with values calculated from vapor pressure data for the reaction $2NbCl_4 \rightleftarrows NbCl_5 + NbCl_3$ as given by Schafer and Bayer (46).

Active Metal Reduction of Halides

The approximate ΔF data in Figures 10, 11 and 12 has been employed with other data from Brewer (10) to give the free energy curves in Figures 13, 14, 15 and 16 for reduction of NbF_5, $NbCl_5$ and $NbCl_3$ by Na, Mg, Ca and Al. Values are not corrected for phase changes of Nb halides.

Obviously there are errors in the basic assumed values, but they are sufficiently good to indicate that all of these reactions are quite favorable from a thermodynamic standpoint as would be expected. In general it can be said that

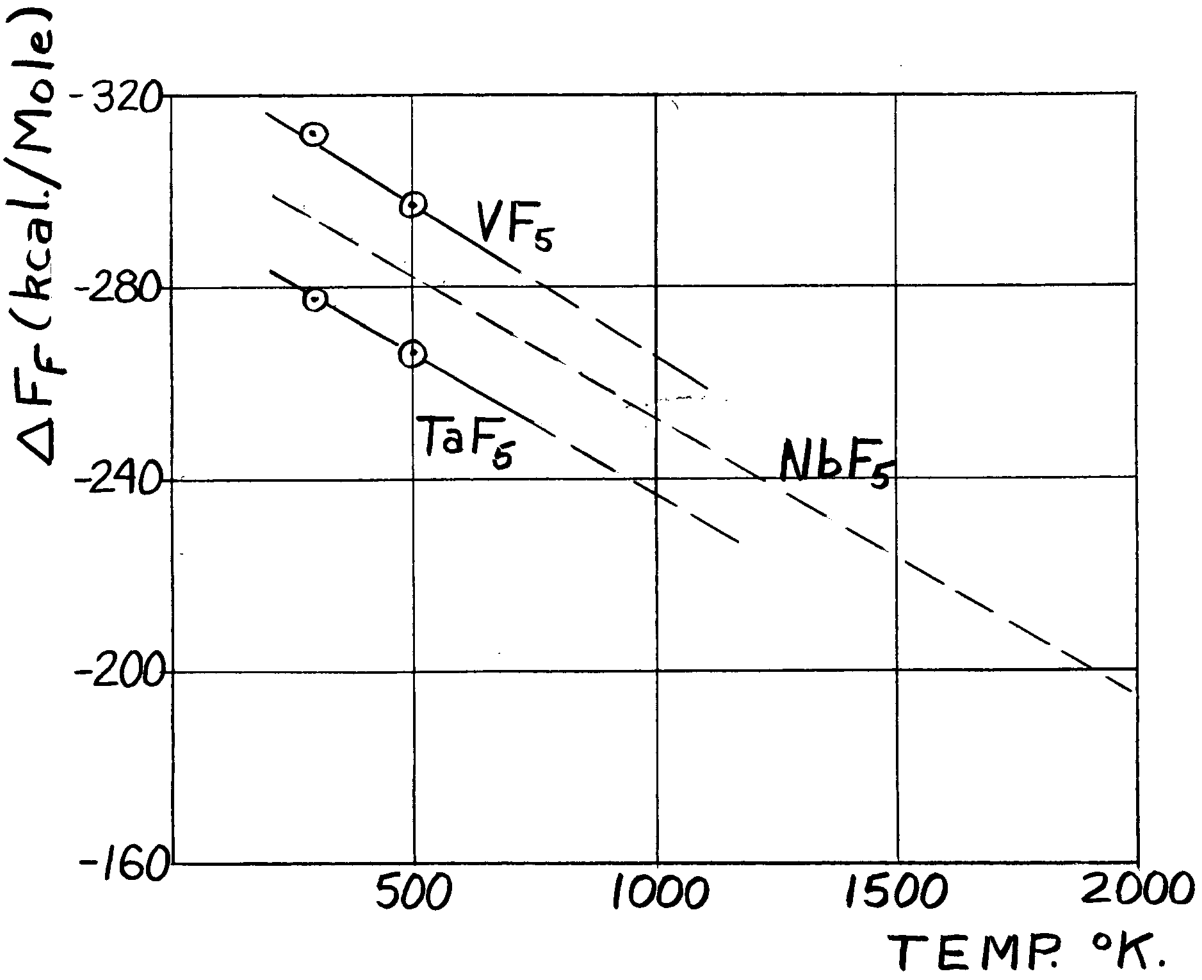


FIG 10
ESTIMATED FREE ENERGY OF FORMATION FOR NbF_5 FROM BREWER ET AL (QUILL)[10]

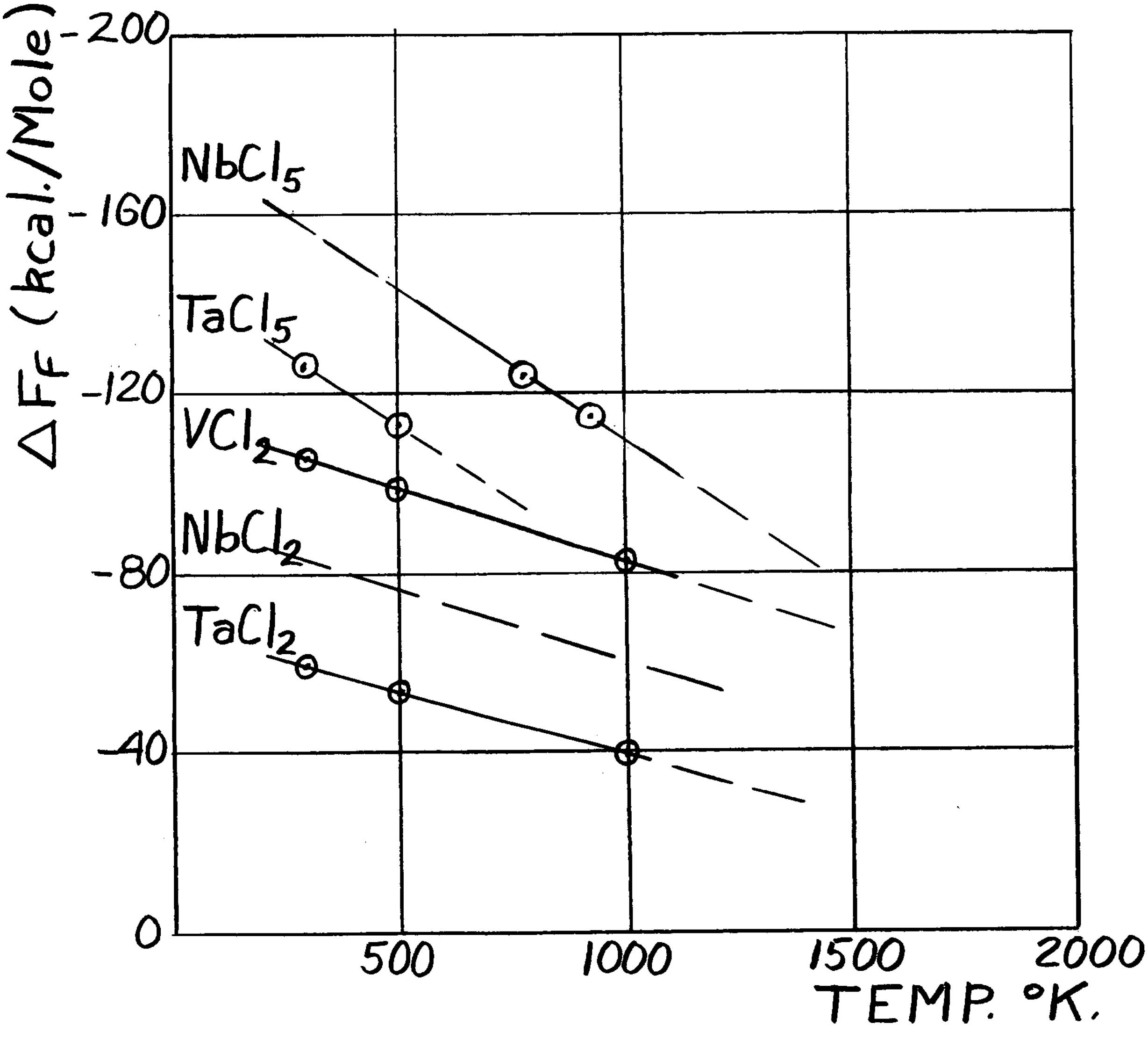


FIG. 11

ESTIMATED FREE ENERGY OF FORMATION FOR $NbCl_2$ AND $NbCl_5$

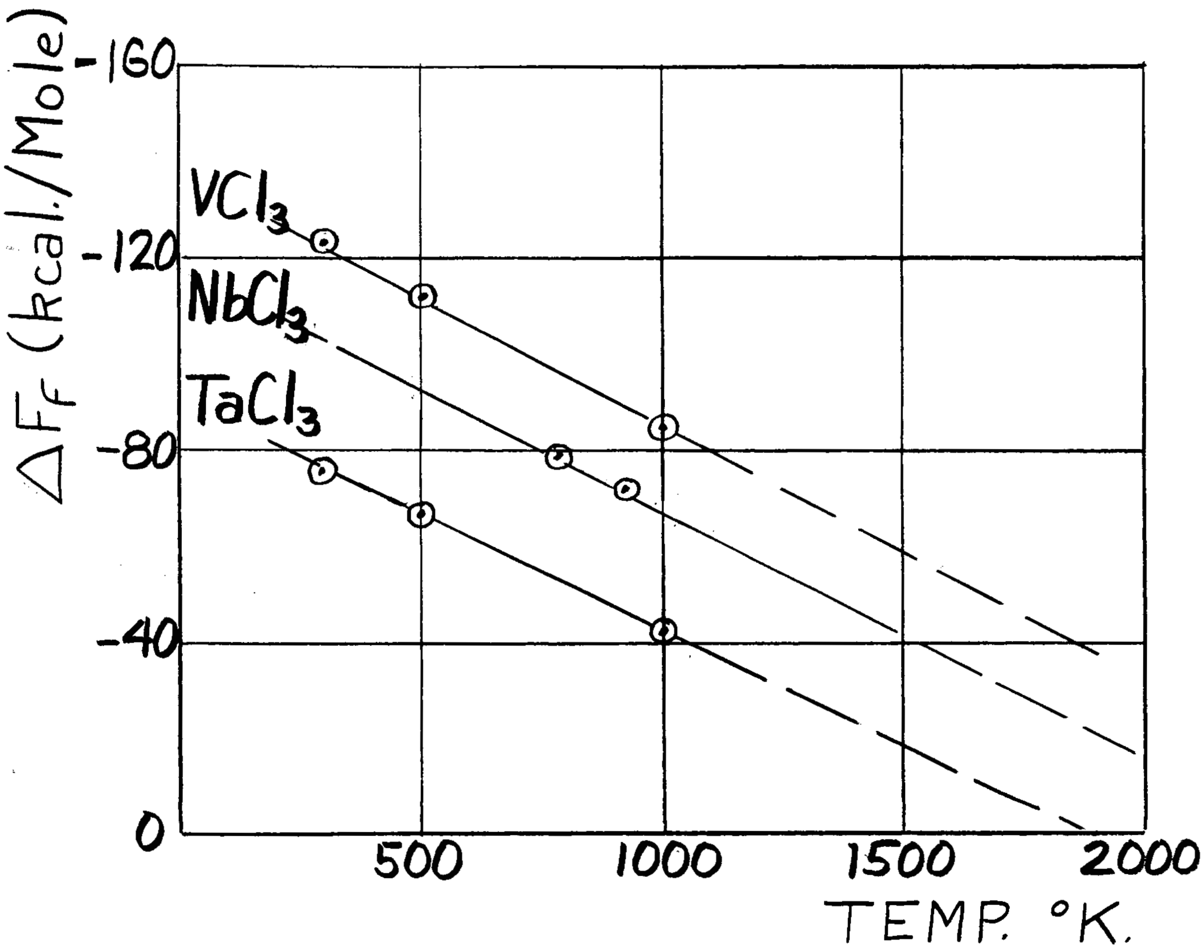


FIG. 12

ESTIMATED FREE ENERGY OF FORMATION FOR $NbCl_3$ FROM BREWER (QUILL)[10] AND MCINTOSH[2]

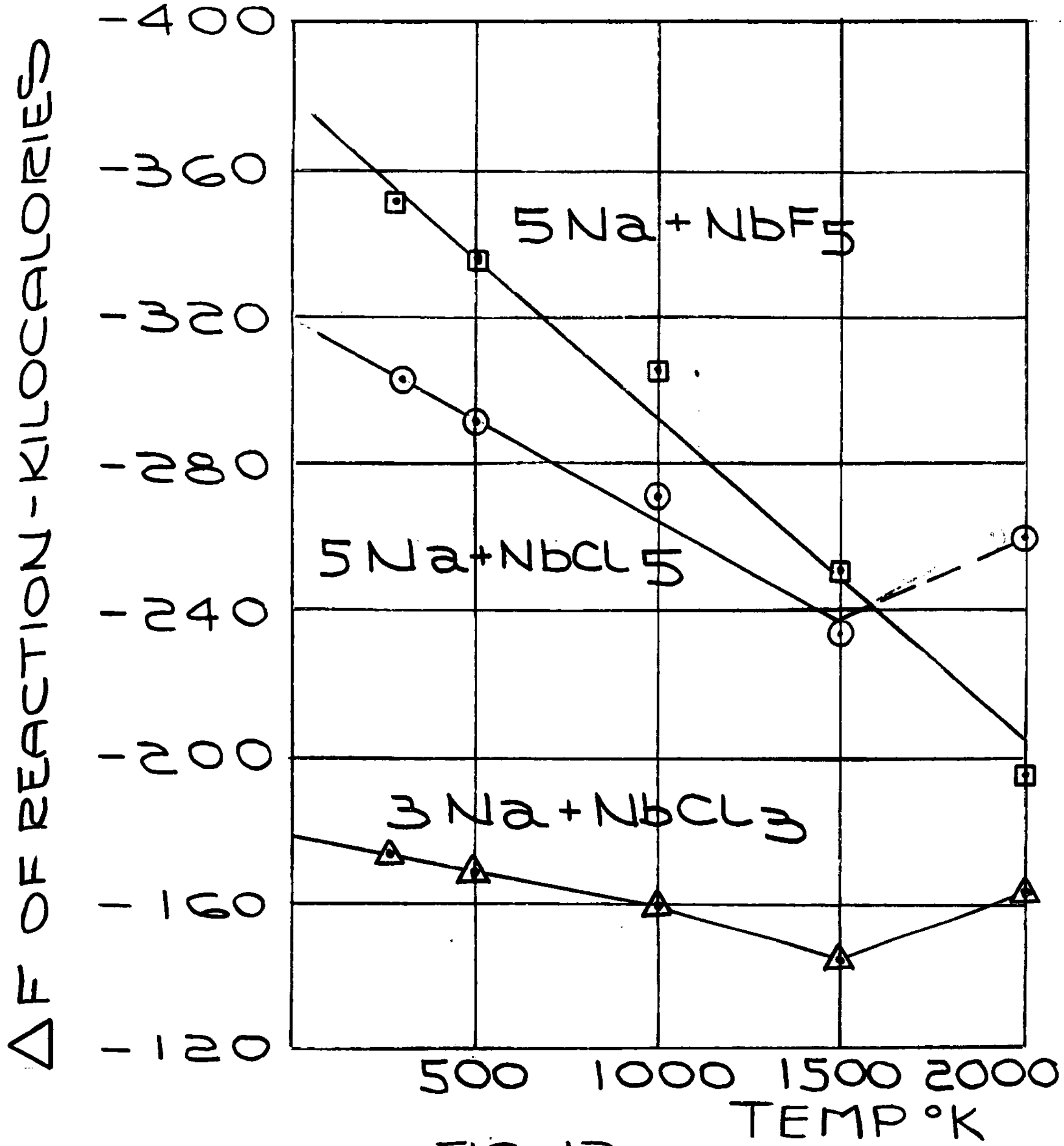


FIG. 13

SODIUM REDUCTION OF NIOBIUM HALIDES

(Data not corrected for vapor phases)

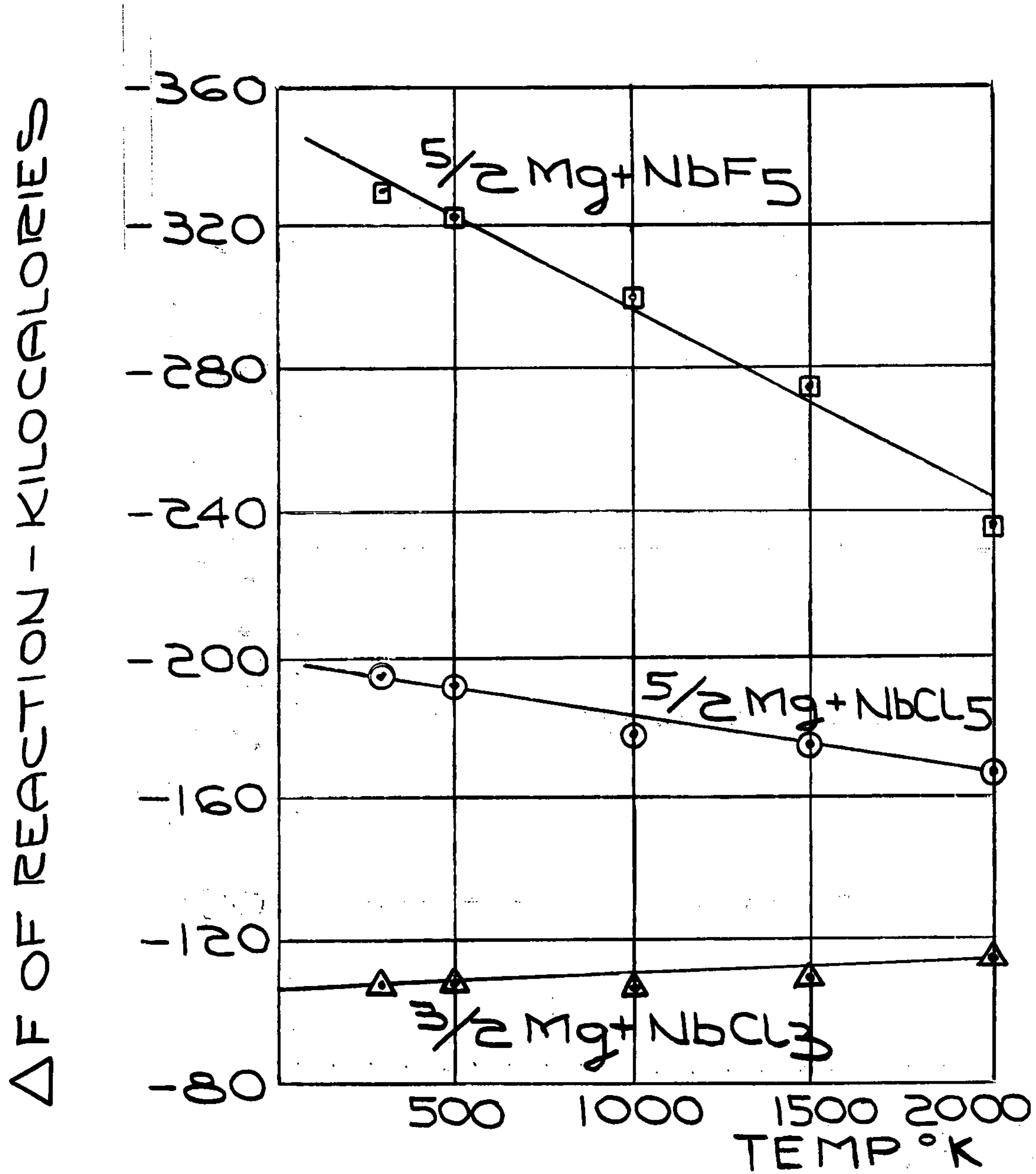


FIG. 14

MAGNESIUM REDUCTION OF NIOBIUM HALIDES

(Data not corrected for vapor phase)

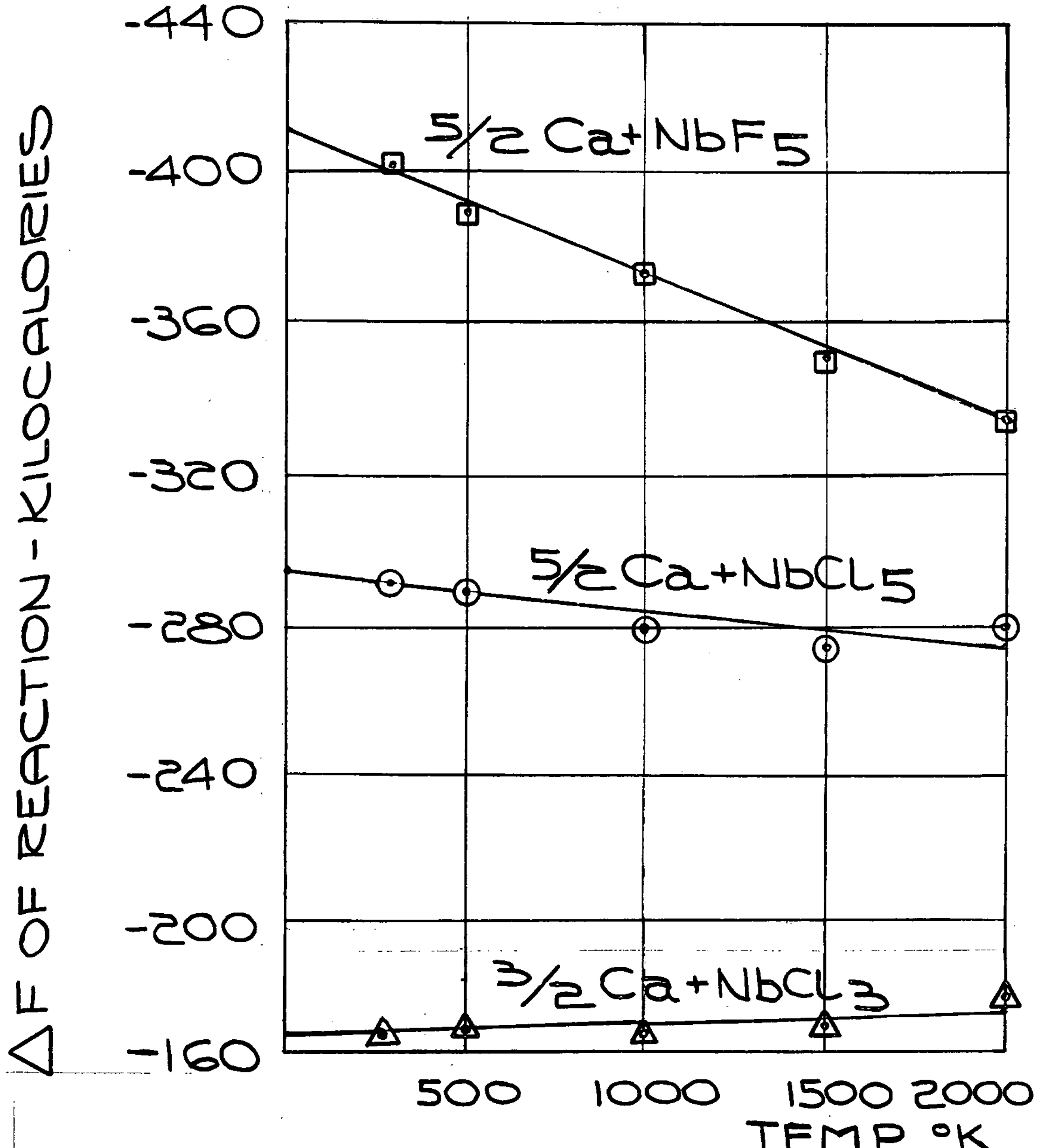


FIG. 15

CALCIUM REDUCTION OF NIOBIUM HALIDES

(Data not corrected for vapor phase)

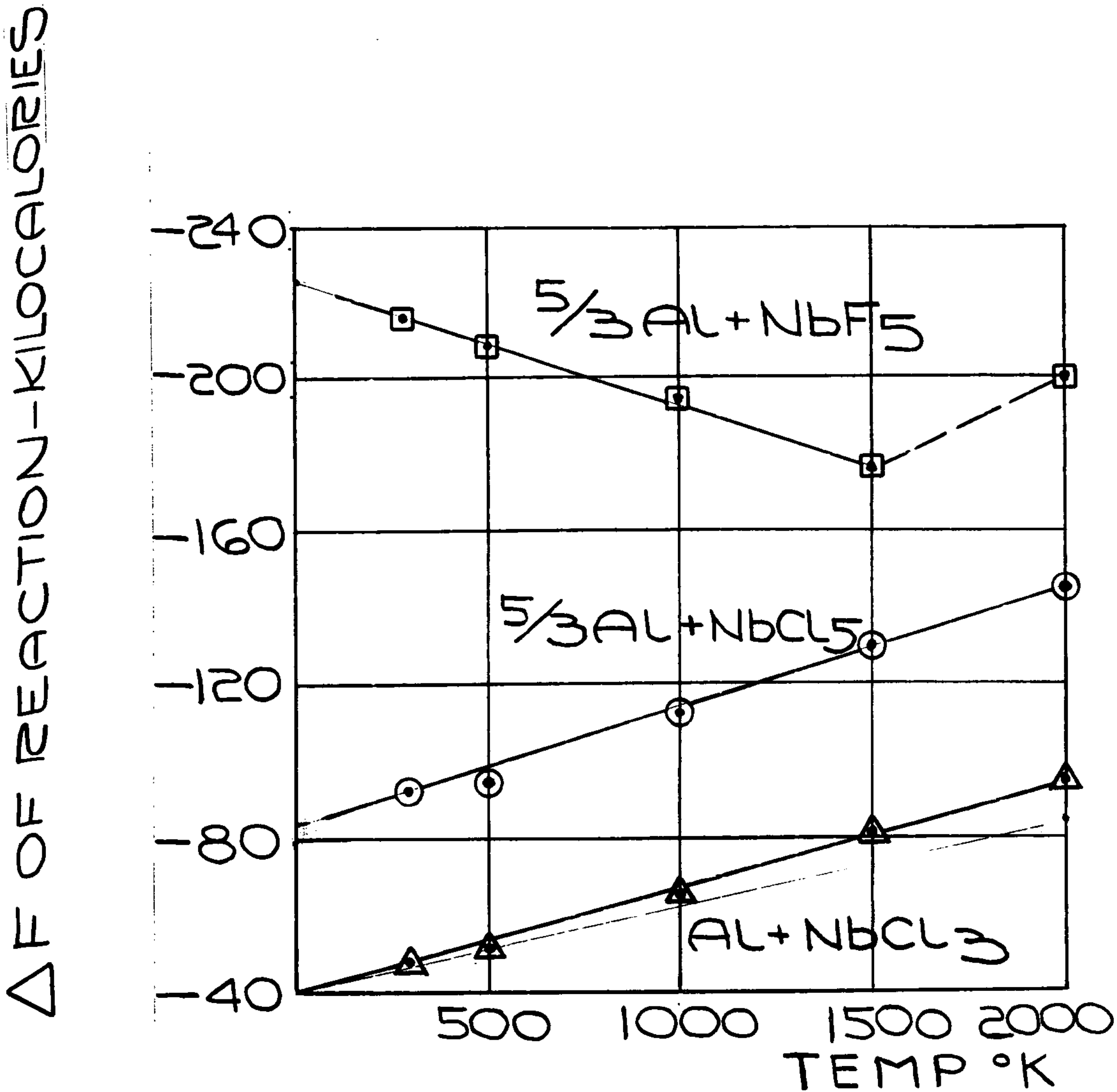


FIG. 16

ALUMINUM REDUCTION OF NIOBIUM HALIDES

(Data not corrected for vapor phases)

chlorides are preferred to fluorides, and Group II active metals to Group I. Although these curves are shown for temperatures up to 2000°K, this type of reaction would probably not be run at more than 1000°K due to the high volatility of both the Nb halides and reducing agents.

The majority of work carried out using the halides as a source of Nb has concerned active metal reduction. A number of such reported experiments are listed in Table V. A number of older references concern the double halides K_2NbF_7 and K_2NbOF_5. Although the efforts of Rose (48), deMarignac (49), and Kruss et al (50), etc., were not successful, it is probable that these reductions could be carried out with improved atmosphere control measures, purity of materials, etc. Von Bolton's Na reduction of K_2NbF_7 (5) was the first recorded preparation of Nb metal. Smithells (51) later prepared a better product by the same method using a sealed bomb.

The pentachloride may be reduced in much the same manner as in the well known Kroll Process for Ti and Zr. Isaza (53) has demonstrated this recently. Other investigators have patented various modifications of this basic reaction including all Nb halides and a variety of reductants, primarily the Group IA and IIA metals plus Al.

Table V

Metallic Reduction of Halides

System	Reference	Conditions	Results
K_2NbOF_5-Na	Rose(1858)(48)		lower oxides
K_2NbOF_5-M	deMarignac(1868)(49)	Zn, Zn·Hg, Fe	lower oxides
K_2NbF_7-Na	deMarignac(1868)(49)		Nb-Na alloy
	Kruss(1887)(50)		Nb-Na alloy
	Von Bolton(1907)(7)		Nb
	Smithells(1931)(51)		
	Dickson(1956)(14)	followed by H_2	pure Nb
K_2NbF_7-Al	deMarignac(1868)(49)		$NbAl_3$ alloy
$NbCl_5$-Na	Glasser(1955)(52)	Na as Na-Hg	pure Nb
$NbCl_5$-Mg	deMarignac(1868)(49)		lower oxides
	Isaza(1947)(53)	KCl flux-10% excess Mg-750 °C	v. fine Nb powd.
$NbCl_5$ or NbF_5-CaH_2 or BaH_2	Gardner(1951)(21)	NbF_5 first sulfided with S or CS_2	
NbX_y-active metal	Rick(1956)(54)	Kroll type process 750-1450 °C	pure Nb
NbX_y-Fe or other metal	Weber(1921)(55)	Volatile halide by-product	Nb
NbX_y-CaH_2-2NaX	Alexander(1956)(56)	> 100 °C slight pressure	Nb

Weber (55) reported the use of Fe as a reductant for Nb halides. Although Nb is much more noble than Ti, Zr, etc., it is doubtful that this reaction could proceed well at nominal reduction temperatures.

Non-Metal Halide Reduction

Relatively little work has been reported on the non-metallic reduction of Nb halides. The only method reported has been hydrogen reduction.

Using the previously deduced ΔF data, free energy of reaction curves for reduction of NbF_5, $NbCl_5$ and $NbCl_3$ by hydrogen were computed as shown in Figure 17. The curve for carbon reduction of NbF_5 is also given. Obviously carbon reductions are out of the question, but the hydrogen reactions are quite favorable. These values are not corrected for phase changes of Nb halides.

This has been substantiated by recently reported work of McIntosh et al (47) who successfully hydrogen reduced the chlorides in 2 steps to give a relatively pure product.

Gonser (58) has patented a plating process involving a similar reaction. Original investigators such as Roscoe (57) obtained only reduced halides, but this was probably due to poor atmosphere control and impure halides. These reductions are summarized in Table VI.

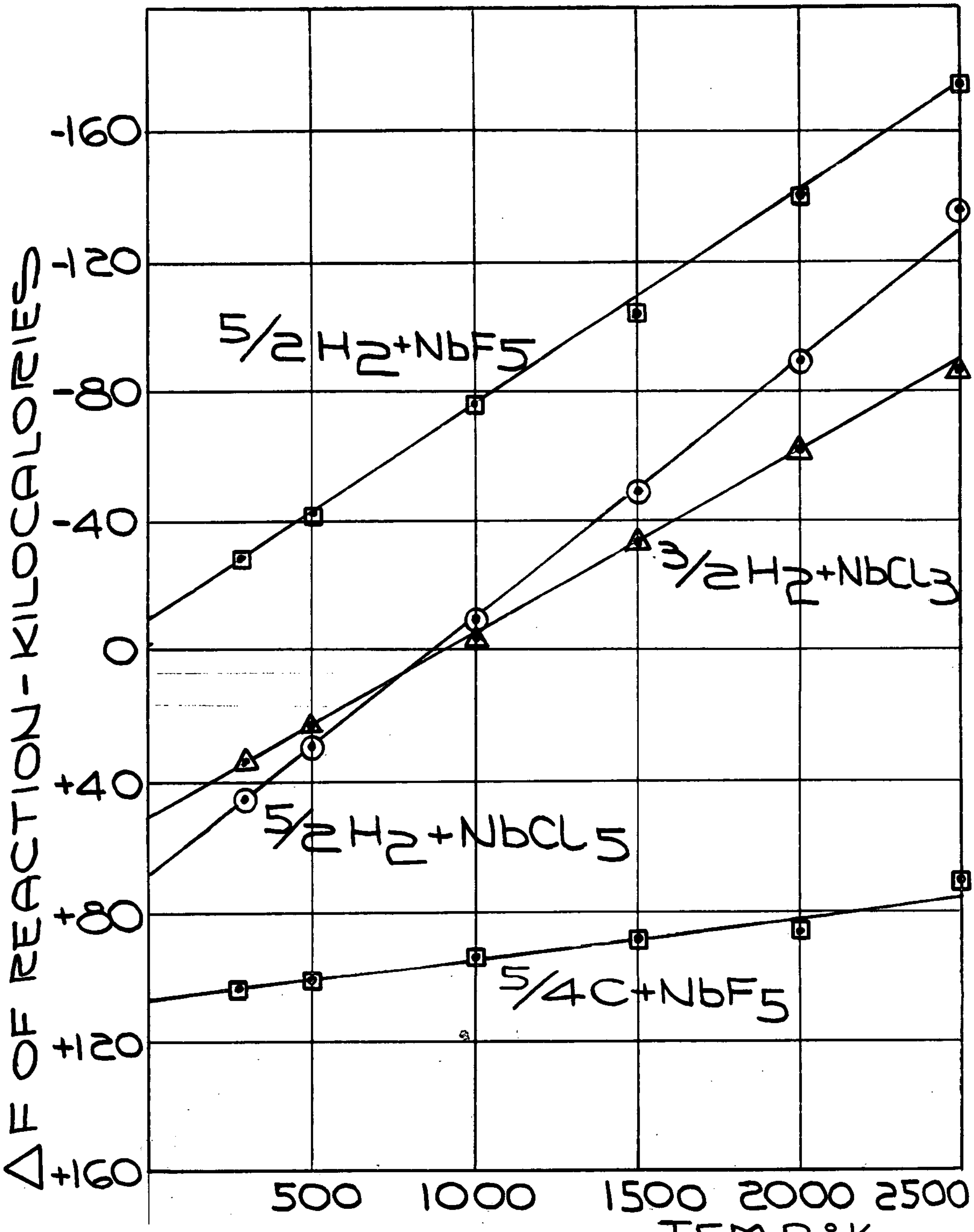


FIG. 17

NON-METAL REDUCTION OF HALIDES

Table VI

Non-Metallic Reduction of Halides

System	Reference	Condition	Results
NbX_5-H_2	Gonser(1952)(58)	500-1300°C-NbX_y(v) over hot base metal	Nb plate on metal base
$NbCl_5$-H_2	Roscoe(1878)(57)		lower chlorides
$NbCl_5$	McIntosh(1956)(47)	500°C	$NbCl_3$
$NbCl_3$-H_2	McIntosh(1956)(47)	> 600°C	pure Nb

It is possible that other non-metals such as silicon could also be used as reductants, but these are not particularly attractive from an economic standpoint.

Electrolytic Reduction of Nb Halides

The only reported electrolysis work with Nb halides has concerned the potassium double fluoride or oxyfluoride largely due to the ease of preparation of these compounds in pure form. The simple halides are difficult to prepare and maintain in a high state of purity due to their extreme hygroscopic and reactive nature.

deMarignac's (49) original electrolyses of the molten oxyfluorides in KF were not successful, but Balke (8)7,8) succeeded in obtaining a metallic product from this material; Nb_2O_5 was added to minimize polarization. Ma (9) also obtained metal from K_2NbOF_5 dissolved in KCl-KF-NaCl in a crystal growth study. Later work at this laboratory (61) duplicates these results, but indicates that the metal so obtained is impure and not ductile.

This and other work dealing with double fluoride electrolysis is listed in Table VII. Driggs (39,40), and workers at this laboratory (61) have used K_2NbF_7 as a source electrolyte in various fused salt mixtures. A very pure

Table VII

Electrolytic Reduction of Halides

Halide	Reference	Melt	Conditions	Product
K_2NbOF_5	deMarignac(1868)(49)	KF(1)	Pt anode	Pt dissolved, no Nb
	Balke(1933)(8)	Nb_2O_5 added	775-1080 A/dm^2-20V	Nb metal
K_2NbOF_5	Ma(1952)(59)	KCl(1)	800°C-20-40 A/dm^2	Nb metal
K_2NbF_7 or other halides	Driggs(1931)(39,40)	NaF-KF(1) or NaCl-KCl(1) w/wo 10% Nb_2O_5	700°C-O_2 at anode	Nb metal
K_2NbF_7	Drossbach(1954)(60)	KCl-KF-NaCl(1)	800°	Nb metal
K_2NbF_7	Horizons(1956)(61)	NaCl, KCl, etc.	650-850°C	high purity Nb
K_2NbF_7	Horizons(1957)(62)	MCl	770-900°C H_2O added to melt	Nb coatings on base metals
K_2NbF_7	Horizons(1957)(63)	MCl	bath purification added	Nb plating

metal product may be prepared in this manner. Two fused salt Nb plating procedures (62,63) utilizing K_2NbF_7 have also been developed in this laboratory.

It is noted that all of these electrolytic procedures employ an alkali chloride or fluoride melt. The reasons for this lie in solubility of the K_2NbF_7 or K_2NbOF_5 in such melts plus the added requirement of a high decomposition voltage salt diluent. E values have been calculated from the ΔF data for NbF_5, $NbCl_5$, $NbCl_3$ and $NbCl_2$ and are shown in Figure 18.

No record of a successful chloride electrolysis has been noted. This is largely due to the low sublimation point of $NbCl_5$ and ease of disproportionation of lower chlorides. $NbCl_2$ is perhaps an exception to this, but little is known of this material. All of the Nb pentahalides have high vapor pressures at temperatures of over 350-400°C making them unsuitable as electrolyte source materials. Vapor pressure curves of the halides from data by Quill (10) are shown in Figure 19. There seems to be little complexing tendency in other melts for the pentachloride.

The only known suitable Nb halide for an electrolytic procedure is K_2NbF_7. This approach offers some promise as a

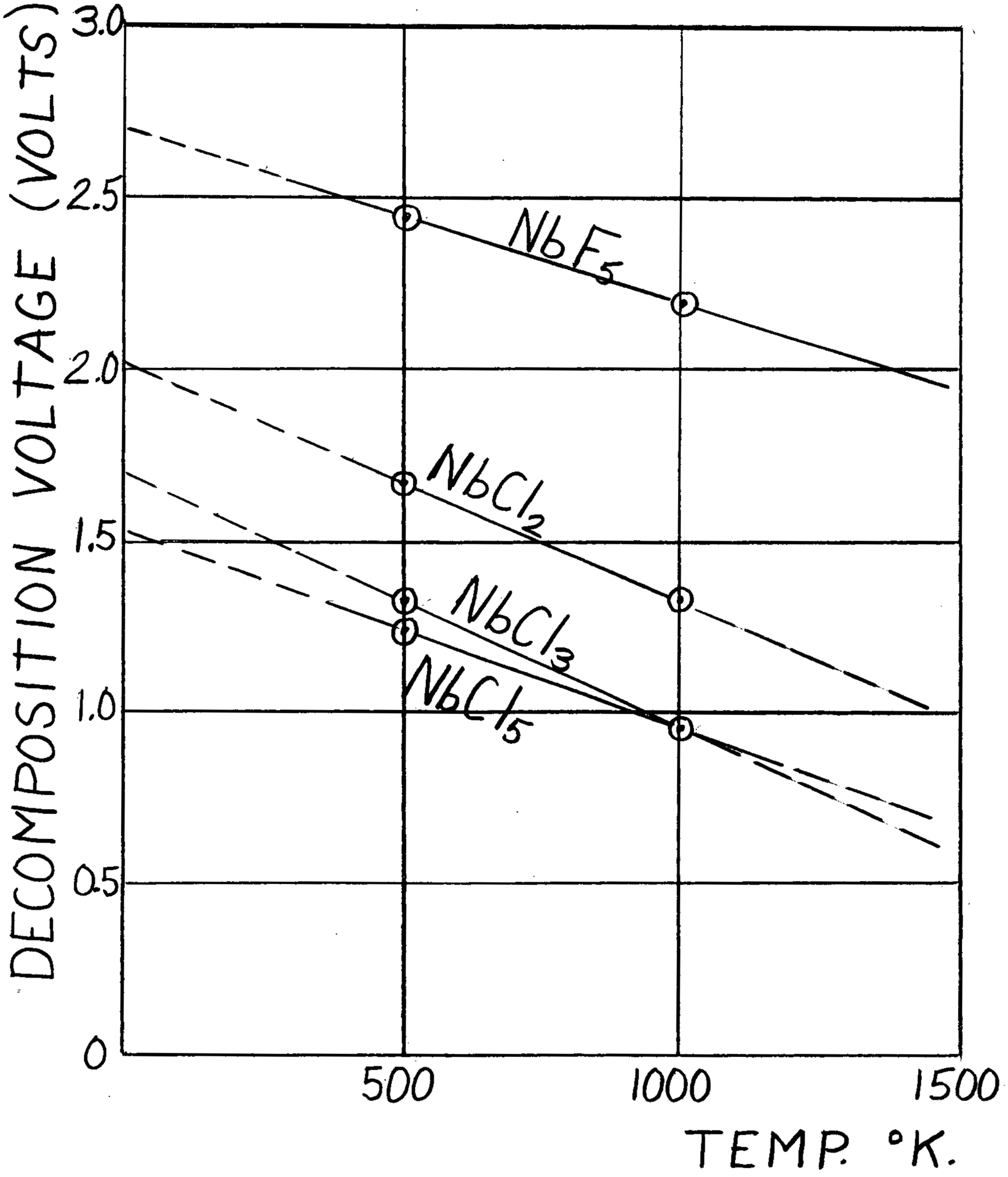


FIG. 18
THEORETICAL DECOMPOSITION
VOLTAGES OF NIOBIUM HALIDES

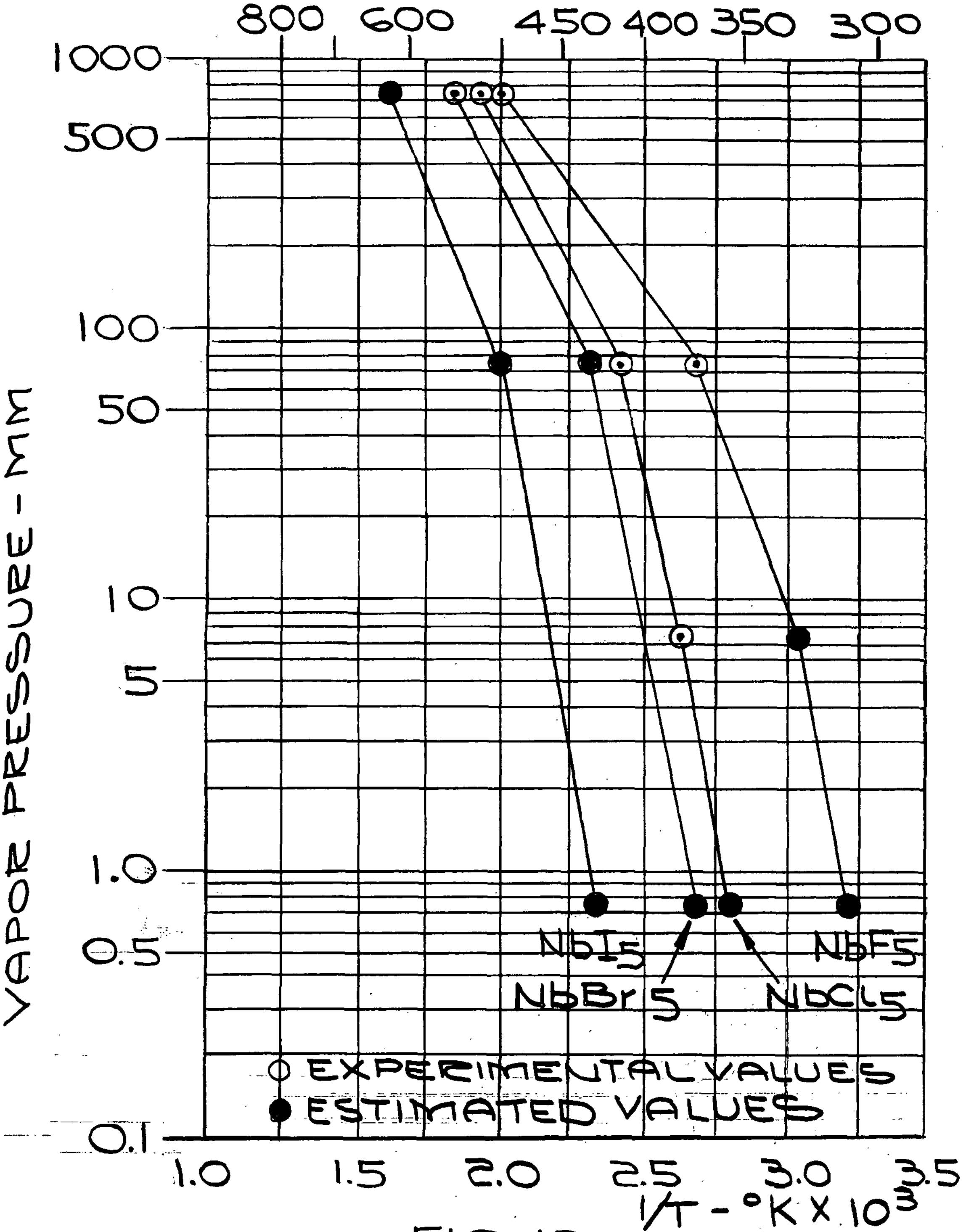


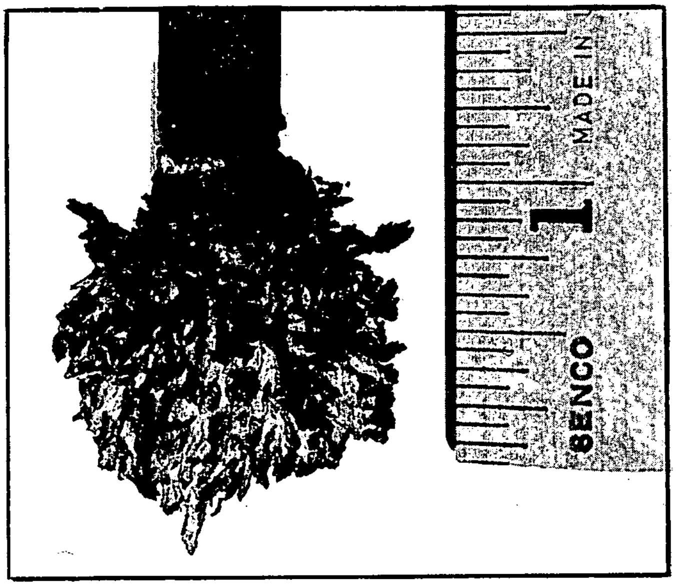
FIG. 19
VAPOR PRESSURES OF NIOBIUM HALIDES

large scale commercial method. Fluoride electrolysis has been used for commercial production by the Fansteel Corp. A typical deposit and high purity Nb crystals from a fluoride melt are shown in Figures 20 and 21.

Electrorefining

One further possible approach to an electrolytic process is a refining method based upon the anodic use of an impure metal in a fused salt melt producing a pure cathodic deposit. Niobium being a relatively noble metal should be amenable to such a procedure. Preliminary work indicates that Nb falls between Cu^+ and Ag^+ in the chloride Emf series and probably just below Fe^{3+}. Thus, at least in a chloride system, elements such as Ti, Zr, V, Cr, Mn and the rare earths should be removed in such a soluble anode procedure. Of course the previously noted problems with regard to development of a suitable chloride melt apply, and experimental observation indicates that there is some question as to transfer of oxygen from anode to cathode in such systems.

The Norton Company has patented a refining procedure (64) utilizing an NbC anode (11.4% C). This laboratory has also patented (65) work on fused halide electrolytic processes employing NbC anodes but problems associated with the melt



Neg. 3300

Figure 20: Nb cathode deposit from electrolysis of K_2NbF_7-NaCl melt.

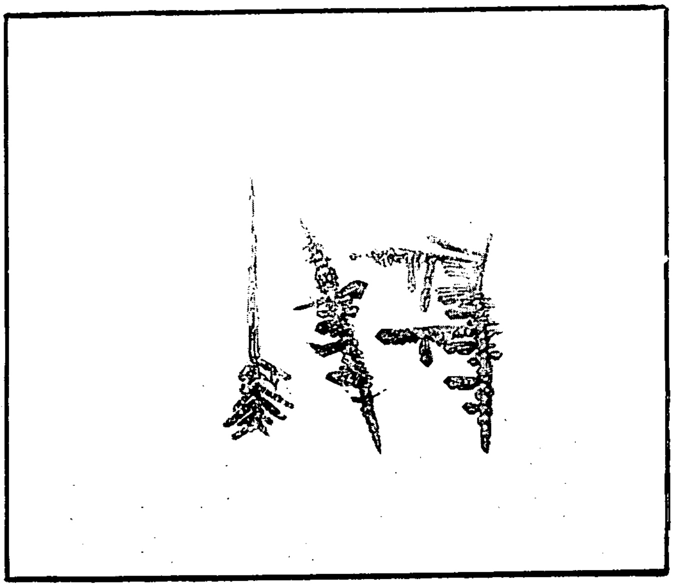


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Figure 21: Typical dendritic electrolytic Nb crystals.

need to be resolved. These approaches are listed in Table VIII. Soluble anode refining processes have been developed for similar metals such as U and Ti.

Disproportionations and Decompositions

Disproportionations and decomposition of halides represent two further potential means for preparation of Nb metal. These apply in particular to the chlorides.

The disproportionation type reaction is a simultaneous oxidation reduction reaction and may be of two types such as:

$$5NbCl_3 \rightarrow 2Nb + 3NbCl_5$$

$$3NbCl_3 \rightarrow 2NbCl_2 + NbCl_5$$

Free energy curves for several such reactions are shown in Figure 22, again based on the original assumed chloride data. It is apparent that all these reactions readily proceed at normal temperatures excepting those of the dichloride which is largely unknown at this time.

Decomposition reactions largely concern only the pentachloride:

$$NbCl_5 \rightarrow Nb + 5/2\ Cl_2$$

It is stated that this reaction starts to take place at about 1300°C (66).

Both disproportionation and decomposition have been

Table VIII

Electrorefining Procedures

Reference	Anode	Melt	Conditions	Product
Horizons(1955)[65]	NbC	Alk or alk earth halides + Nb halide	700-1000°	Nb metal
Norton(1956)[64]	NbC	Alk or alk earth halides		Nb metal

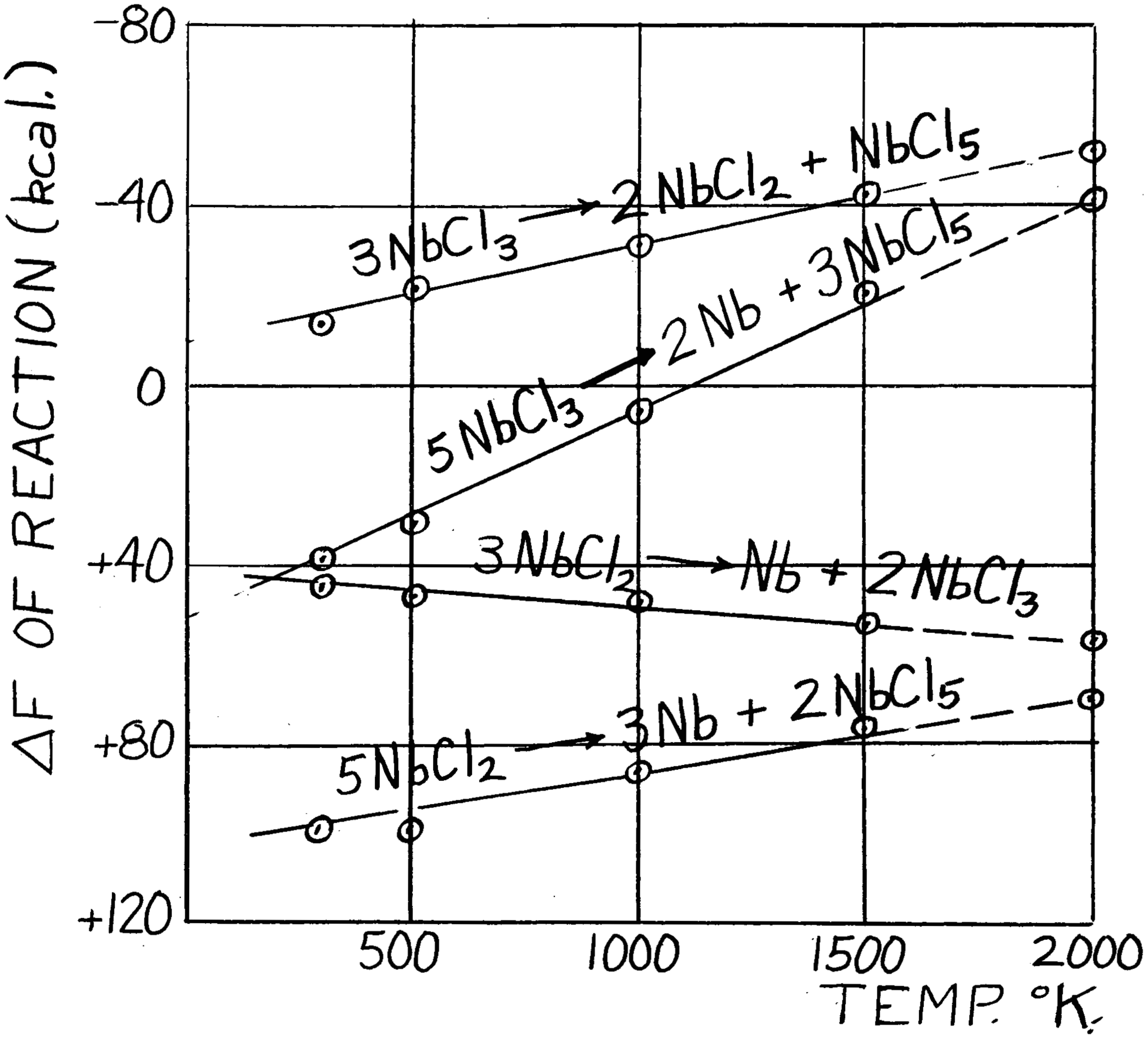

FIG. 22
DISPROPORTIONATION REACTIONS OF NIOBIUM CHLORIDES

proposed as approaches to preparation of the metal. Several such references are noted in Table IX, along with some miscellaneous processes of similar principles of operation. Aylsworth (67) proposed the first such Nb process for preparing filaments whereby Nb halides were decomposed on a hot wire in a hydrogen atmosphere. Heany (22) reported a similar method except that instead of volatile halides, nitrides and hydrides were specified. Powell (69) further developed the hot wire process based on the Van Arkel iodide process for Ti and Zr. Gonser (58) used similar methods for Nb plates on base metals, decomposing the halide on a heated base metal plate.

Begley (66) has proposed the direct decomposition of $NbCl_5$ as a purification process for Nb. Van Arkel (68) has also discussed dissociation methods in detail.

$$NbCl_5 \underset{300^\circ}{\overset{1300^\circ}{\rightleftarrows}} Nb + 5/2\ Cl_2$$

Austin (70) formed the hydride NbH_2 from scrap Nb, then ground and decomposed it in a vacuum to give pure Nb.

In addition to their potentialities as methods of preparation, disproportionation and decomposition reactions present serious problems particularly in the development of fused chloride melts for electrolytic processes. The

Table IX

Other Processes

System	Process Type	Reference	Remarks	Results
NbXy-H_2	Hot wire-H_2 reduction	Aylsworth (1896)(67)	vessel and wire both heated	Nb deposit
NbN, NbH_2	Decomposition	Heany (1907)(22)	used for filaments	Nb
Nb halides	Dissociation	Van Arkel (1934)(68)	vacuum high temp.	Nb
Nb halides	Hot wire process	Powell (1948)(69)	Nb wire	v. pure Nb
Nb halides	Decomposition	Gonser (1952)(58)	Decomp.on metal plate in H_2 500-1300 °C	pure Nb
$NbCl_5$	Decomposition	Begley (1956)(66)	Decomp. at 1300 °C	Nb
Nb Scrap-H_2	Hydrogenation of scrap	Austin (1938)(70)	hydride formed, heated in vac.	pure Nb
Impure Nb	Purification by sintering	O'Driscoll (1957)(71)	sintered at 1700-2300 °C high vac.	pure Nb

pentachloride is not suitable above 400°K due to its high vapor pressure (see Figure 19). It is apparent from Figure 22 that $NbCl_3$ is unstable toward disproportionation under all conditions. The dichloride should be stable if it could be readily prepared in a fused melt.

In addition to fluorides, the dichloride is probably the most promising material for a fusion electrolysis process. The unexplored area of bromides and iodides might be useful in soluble anode procedures where constant concentrations are employed.

Conclusions

Nine possible approaches to the preparation of niobium metal have been briefly considered based on theoretical considerations and experimental work. These include reduction of oxides and halides by active metals, non-metals and electrolysis, electrorefining, disproportionation of chlorides and decomposition of chlorides. Such methods largely parallel processes in use or proposed for other refractory transition metals.

None of the oxide reduction methods show any great promise as commercial one-step processes for production of pure metal. Although thermodynamic considerations indicate active metal and carbon reductions to be favorable, kinetic considerations and by-product separation problems complicate the picture considerably. The NbC-Nb_2O_5 reduction is used commercially to a small extent.

Electrolytic processing of Nb oxides offers little promise from any standpoint due to the oxyphillic nature of Nb and its ions. It is apparent that any eventual process for high purity Nb must be carried out in the absence of oxygen and oxy-ions. This disqualifies all aqueous and most possible organic media. Metal of 99% and greater purity is prepared from K_2NbOF_5 and K_2NbF_7-Nb_2O_5 melts, but this product is not satisfactory for many anticipated applications.

The most promising area of processing appears to involve halide reduction. It is apparent that alkali metals, alkaline earth metals, aluminum and even hydrogen can reduce $NbCl_5$ and NbF_5 to metal, and experimental evidence indicates that high purity materials can be so obtained. Certain problems exist due to the low sublimation point of $NbCl_5$, disproportionations, etc., but these can eventually be circumvented by new techniques and design.

Electrolytic processing of halides is perhaps the most interesting area of development. The utility of fluoride baths has been adequately demonstrated, but these melts are not readily amenable to continuous processing. Chloride melts entail problems, particularly in disproportionation. Use of very low temperature, highly reduced melts or suitable complexing agents could overcome these problems. Bromides and iodides have not been considered due to their high cost of preparation and the lack of knowledge of their chemistry.

A further electrolytic approach of interest is electrorefining wherein an impure metal product might be utilized as an anode material in a fusion electrolysis. Successful processes of this type have been developed for Ti, Zr, U, etc.

Disproportionations are not too promising as processing methods. These reactions are difficult to control and a variety of products are present at all times since more than one reaction is generally involved.

The proposed decomposition methods are not encouraging either. The Nb halides are reasonably stable toward decomposition to metal and gas. High temperatures required, low yields and serious contamination by lower halides would be expected.

At the present time, new process development for Nb would logically be expected to follow that of similar metals.

New processes will likely evolve in the areas of halide reductions by either metallic, hydrogen or electrolytic means.

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