



Trends in the Use of Vanadium (1970)

Pages
59

Size
8.5 x 10

ISBN
0309344867

Panel on Vanadium; Committee on Technical Aspects of Critical and Strategic Material; National Materials Advisory Board; Division of Engineering; National Research Council

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TRENDS IN THE USE OF VANADIUM

**REPORT
of the
PANEL ON VANADIUM**

**COMMITTEE ON TECHNICAL ASPECTS OF
CRITICAL AND STRATEGIC MATERIALS**

**NATIONAL MATERIALS ADVISORY BOARD
DIVISION OF ENGINEERING--NATIONAL RESEARCH COUNCIL
#**

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Publication NMAB-267

**National Academy of Sciences - National Academy of Engineering
Washington, D. C.
March 1970**

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I. SUMMARY OF TRENDS IN THE USE OF VANADIUM

A large number of traditional uses of vanadium as a minor addition to a variety of tool steels, stainless steels, engineering alloy steels, special alloys, and cast irons will continue for sound technical reasons. The growth in use will be modest. Substitution for vanadium is possible in every case, but inertia is against such a trend except under the pressure of severe shortage.

Two relatively young segments of the steel industry (high-strength, low-alloy steels (HSLA) and continuous casting of steel slabs and billets) are likely to exceed all other cumulative uses of vanadium. In fact, if the demand predictions are reasonable, vanadium production may be taxed to keep pace. Of these growing uses, the HSLA steels make the biggest demand and seem to have a strong basis for preference for vanadium. Columbium is a substitute but, from various viewpoints, would not be preferred except during periods of vanadium shortage or a substantial price rise in vanadium.

A continued use of vanadium in titanium alloys is predicted so that increasing demand for vanadium will be proportionate to the growth of the titanium industry.

It is simply not possible to predict reliably the need for vanadium as a fuel element cladding in the fast breeder reactor. There is clearly a competition between vanadium alloys and molybdenum. Indeed, with proper trade-offs and engineering design modifications, the currently referenced austenitic stainless steels may prove to be adequate. None of these materials is ideal in every respect, so that the final choice must be made on the basis of which is the least undesirable. This decision is some years off. Moreover, if the decision favored vanadium alloys, the demand on a large scale is perhaps 15 years off.

Table 1 summarizes the projected United States needs for vanadium in all major categories for the year 1975. This has necessitated some

interpolations and some modest extrapolations from the various sources of information.

If a significant need develops for vanadium for nuclear reactors, the present stockpile of vanadium pentoxide may be unsatisfactory. Its procurement specification did not restrict the contents of deleterious elements such as nitrogen and boron.

TABLE 1
SUMMARY OF UNITED STATES DEMAND FOR VANADIUM
PROJECTED FOR 1975

<u>Use</u>	<u>Amount (Thousands of pounds)</u>	<u>Origin of Figure</u>
Tool steels, stain- less steels and special alloys	1,560	1968 figures compounded at 2%
Engineering alloy steels	1,250	Extrapolated from Table VI
High strength low alloy steels	12,650	Extrapolated from Table IX
Continuous cast steel slabs	1,000 - 3,700	Extrapolated from Table X
Continuous cast steel billets	530 - 6,000	Extrapolated from Table XI
Cast iron	1,000	Extrapolated from Table XIV
Titanium alloys	2,650	Figure 1, text
Chemical applications	<u>400 - 500</u>	Statement in the text
Total for year 1975	21,040 -31,240	

II. INTRODUCTION

Vanadium has a long history of use as a minor addition to steel and as a catalyst in certain chemical reactions. Generally, vanadium is not used as the metal. For alloying purposes, it is commonly supplied as a master alloy, such as ferrovanadium or vanadium-aluminum, and for chemical purposes, it is supplied as a compound, such as V_2O_5 . More recently, a variety of steel and titanium alloys have increased their usage substantially. In these alloys, small additions of vanadium confer very advantageous strength characteristics. The use of vanadium is likely to exceed the increases predicted from over-all projected national production expansion.

Vanadium, as a metal or base for alloying, has had a frustrating history. It is well within present technology to produce a metal of sufficient purity to allow fabrication to any useful shape. It is highly formable and can be welded satisfactorily. Corrosion resistance in many media is good but not outstanding. As a pure metal, its strength is modest. By solid solution alloying, considerable strengthening with preservation of adequate ductility is possible. Its high-temperature strength is substantial up to 1800°F . However, it has a serious oxidation resistance problem. Above 1250°F ., the oxide V_2O_5 melts and the oxidation process becomes linear, i. e., vanadium loses its ability to maintain a protective oxide coating in an oxidizing environment. Vanadium arrived too late on the scene to compete with titanium in jet engine and airframe applications. Because of its scale of production, the cost factor does not look favorable. The brief interest in vanadium as an interliner in titanium-clad steel died with the advent of explosion welding which apparently solved that problem. Now, the only outstanding future application under consideration is as a cladding material for the fuel element in a new generation of breeder reactors. If this use is realized, its ultimate consumption would be large, but this probability depends upon the weight attached to what is known about vanadium and not known about its competitors, such as molybdenum.

The exploitation of vanadium resources has changed rather abruptly over the past twenty-five years. Once the major source, the asphaltite deposits of Peru are essentially exhausted. In recent years, the proportion of vanadium as a co-product of uranium extraction has been a decreasing proportion of the United States output. However, this source and the vanadium mined in Arkansas are the largest components of this country's production. In the future, apparently, the largest source of vanadium will be the vanadium-bearing slags, a by-product of iron production which uses certain iron ores containing a small percentage of vanadium. As such, the economies and output of vanadium will be closely tied to the economies of iron production from these various deposits.

The extraction processes for vanadium follow a common pattern. First, the mineral content is converted to a soluble form by salt roasting. After leaching this product, the valuable elements are selectively precipitated. The vanadium product is a sodium vanadate which, after drying and fusing, contains 85-90 weight percent V_2O_5 , known as commercial vanadium oxide. A pure V_2O_5 can be manufactured by forming and decomposing ammonium metavanadate. Commercial vanadium oxide is the starting material for reduction operations producing ferro-vanadium, vanadium-aluminum, and more complex products, that serve as the alloy additions in various applications to be described in this report.

III. RESOURCES AND SUPPLY OF VANADIUM MATERIALS

The major sources of vanadium in the past have ranged from the Mina Ragra area of Peru (1906-1940) to the Colorado plateau (1940-1968) and now to the Bushveld complex in the Transvaal of the Republic of South Africa, the Wilson Springs, Arkansas, area, and the ore bodies of the Russian Ural mountains. The type of natural occurrence which yields the major quantities of vanadium has also changed from an asphaltic material in Peru to roscoelite and carnotite ores in Colorado, Utah, and Arizona, to descloizite and other lead and zinc vanadates from southwest Africa, titaniferous magnetites from the Transvaal and the Urals, and vanadiferous clays from central Arkansas. See Table 2.

TABLE 2

COMMON VANADIUM-BEARING MINERALS

<u>Mineral</u>	<u>Chemical Composition</u>
Patronite	Vanadium sulphide (VS_4 or V_2S_5)
Descloizite	Lead-zinc-vanadate
Cupro-descloizite	Copper-lead-zinc-vanadate
Mottramite	Copper-lead-zinc-vanadate
Vanadinite	Chloro-lead-vanadate
Carnotite	Uranium-potassium-vanadate
Roscoelite	A mica containing vanadium pentoxide in solution
Tyuyamunite	Uranium-calcium-vanadate
Phosphate rock	

Quantities of vanadium are also obtained from phosphate rock in Idaho as a by-product of phosphorus production, from vanadium-rich slags from vanadiferous magnetite ores in Chile as a by-product of steel production, and from residues of Venezuelan crude oils. The Bureau of Mines estimates of world mine production in thousands of pounds of contained vanadium and reserves are summarized in Table 3.

Apparently, the major sources of vanadium in the future will be titaniferous magnetite containing small percentages of vanadium. Present and possible future sources are listed in Table 4. (This is not a complete list but is an attempt to show many of the important ore sources now known.)

In the near future, the largest source of vanadium will derive from titaniferous magnetite from the U. S. S. R. and South Africa. Except for small percentages of the world's supply that will come from tar sands, clays, phosphorus recovery, titanium and uranium recovery, and oil residues, apparently future vanadium demand will be satisfied largely by existing and new installations designed to produce vanadium as a co-product of steel manufacture.

The production of vanadium as a co-product of uranium has been proven economically attractive. Increased prospecting activity to locate sources of uranium, if successful, may also play a large part in future vanadium supply.

IV. CONSUMPTION BY APPLICATION

A. Vanadium in Tool and Die Steels

Of the vanadium consumed in the manufacture of tool and die steels, the high-speed steels (AISI M and T types) account for 70%. These steels are used for the manufacture of tools employed in metal removal operations such as cutting, drilling, hobbing, and reaming. Vanadium is an essential element in all common high-speed steels and is present from 1 to 4%. A major portion of the vanadium is found in the carbide phase after hardening; first, the vanadium

TABLE 3

WORLD MINE PRODUCTION AND RESERVES

	<u>Mine Production*</u>		<u>Reserves</u>
	<u>1967</u>	<u>1968</u>	
United States	9926	12966	Moderate
Republic of South Africa	4230	4996	Large
Other Free World (Norway, Finland, South- west Africa, etc.)	6862	7162	Moderate
Communist Countries (Except Yugoslavia)	N. A.	N. A.	Large
Free World Total	21018	25124	-

* Thousands of pounds of contained vanadium

TABLE 4
WORLD RESOURCES OF VANADIUM

<u>Country</u>	<u>Site</u>	<u>Ore Type</u>	<u>V₂O₅ Content-%</u>	<u>Known Resources Millions of lbs. of V</u>	<u>Inferred Resources</u>	<u>Status</u>
U. S.	Wilson Springs, Ark.	Vanadiferous clays	0.7-1.3	Unknown	Unknown	Being worked for V only
U. S.	Colo., N. Mex., Utah & Ariz.	Carnotite and Roscoelite	0.1-0.5	35	70 million lbs. of V	Being worked for U and V
U. S.	Black Hills, S. Dak., & Wyo.	Carnotite	0.2-0.5	0.9	3 million lbs. of V	Inactive
U. S.	Idaho	Phosphate rock	0.2-0.3	Unknown	Large	Being worked for P and V
U. S.	Idaho & Wyo.	Vanadiferous shales	0.7-1.25	600	Very large	Inactive
U. S.	Lake Sanford, N. Y.	Titaniferous magnetite	0.45	600	None	Being worked for Ti only
U. S.	Iron Mtn., Wyo.	Titaniferous magnetite	0.4	36 min.	Very large	Inactive
U. S.	Duluth, Minn.	Titaniferous magnetite	0.5-2.6	1000	None	Inactive
U. S.	Iron Mine Hill, Rhode Island	Titaniferous magnetite	0.3	42	None	Inactive
TOTAL U. S.				2354+		
Canada	Quebec & Ont.	Titaniferous magnetite	0.5	Unknown	Unknown	Inactive
Canada	Alberta	Athabasca tar sands	240 ppm in the tar (4% in ash)	Unknown	Unknown	Being worked-- V-bearing fly ash stockpiled
Canada	Montreal	Petroleum residues	230 ppm in crude	0.2/yr.	Unknown	Being processed

Canada	Chibougamau, Quebec	Magnetite & ilmenite	0.5		Very large	Unknown	Inactive
Chile		Magnetite	0.4-0.7		3500	Unknown	Being worked for steel & a small quantity of V
Venezuela		Crude oil	230 ppm in crude		Unknown	Unknown	Being processed
Southwest Africa	Berg Aukas	Lead-zinc vanadates	1.6		8	Unknown	Being worked
Rep. of S. Africa	Transvaal	Titaniferous magnetite	1.5-2.0		4000	Very large	Being worked
Australia	Jameson Range	Titaniferous magnetite	1.5		None	3000	Inactive
USSR	Mt. Kachkanar	Titaniferous magnetite	1.25		Unknown	Unknown	Being worked for steel & V
India	Bihar	Titaniferous magnetite	2.0		880	None	Under development
India	Mysore	Titaniferous magnetite	Unknown		Unknown	Large	Inactive
Finland	Otanmaki	Magnetite-ilmenite	1.0		250	Unknown	Being worked
Sweden	Kiruna, Taberg	Titaniferous magnetite	0.2		5	Unknown	Being worked for steel and V
Norway	Ekersund	Titaniferous magnetite	Unknown		Unknown	Very large	Being worked for steel and V
China	Jehol, Manchuria	Titaniferous magnetite	0.2		12	Unknown	Probably being worked
Japan		Beach sands	0.4		Unknown	Large	Inactive
New Zealand	North Island	Beach sands	0.4		Unknown	Very large	Being worked for steel

* Information for the table is taken from "Vanadium--A Materials Survey," P. M. Busch, Information Circular 8060, U.S. Bureau of Mines, private communication from R. P. Fischer of the U.S. Geological Survey, and assorted published information.

Rev. 9/17/69

aids in maintaining a fine austenite grain size during solution heat treatment, and then, remains as a hard, wear-resistant constituent which improves performance in subsequent cutting operations. A small percentage of vanadium that is dissolved in the austenite reprecipitates as a fine carbide during tempering, thus assisting in maintaining hardness and strength at elevated temperatures. The importance of vanadium can be judged from the fact that no vanadium-free high-speed steels are in use.

Cold work steels are used in a wide variety of applications: wrenches punches, arbors, shock-resistant pneumatic tooling, blanking and perforating die sets, accurate gages, and thread rolling dies. In the AISI S, A, and O types typically .2/.3% vanadium is contained in the analysis, although a 4.5% vanadium A type is available. This low vanadium, present mostly as a fine-dispersion of vanadium-carbide particles, is primarily for the purpose of keeping the austenitic grain size fine during hardening. A fine grain size is necessary to provide maximum toughness at a given hardness.

The high-carbon, high-chromium AISI D series contains two widely used steels alloyed with vanadium. The 1% vanadium alloy, D2, has wide application in flat thread rolling dies, blanking dies, and coining dies. The 4% vanadium steel (D7) is used in extremely abrasive applications, such as brick and concrete block manufacturing and shot-blasting chamber liners, the additional vanadium forming the hard primary carbide particles which provide for the striking improvement in wear resistance.

The hot-work steels, such as those used in die casting metals and in hot-forming operations, contain vanadium at two distinct levels, .3%/.5% or 1%. At the .3%/.5% level, the vanadium assures fine grain size during heat-treatment, as explained above, and provides for some heat-resistance. The higher vanadium level (1%) provides a slight improvement in wear without adverse effects upon toughness. As with the cold-work steels, several specialized compositions containing 2.5% or 4% vanadium (with corresponding higher carbon) have been developed for extreme wear applications.

The consumption of vanadium by tool steel product groupings is given in Table 5. The market for tool and die steels has become very stable and future growth is predicted to be in step with the economy. A steady expansion of about 2% compounded is expected in the next five years for the various tool and die steels, including the high-speed steels. These alloys are so well established that no substantial change in the pattern of vanadium consumption is expected, at least over the next few years.

Since the inception of tool steels, vanadium has been added primarily for grain size control, and then, for the imparted extra hardness and wear-resistance. Vanadium can be added during normal melting in electric arc furnaces with good recovery, as it is not a strong oxide former. Titanium, zirconium, columbium, and tantalum (the last two are frequently in combination) have very similar metallurgical properties, and might have possibilities as substitutes for vanadium in tool steels. However, the solubility of their carbides in austenite is even more limited than vanadium-carbide, and thus the temper resistance would be reduced. A further drawback to the use of titanium and zirconium is their reactivity with oxygen. Accordingly, vacuum melting is required for their effective recovery.

For some time the possibility of substituting columbium for vanadium was dim since the cost of columbium was about $2\frac{1}{2}$ times higher than the metallurgical equivalent of vanadium. At present, however, vanadium has been increasing in price, while the price of columbium has remained relatively stable.

B. Vanadium in Stainless Steels

The stainless steels are widely known for their corrosion resistance and pleasing appearance. Actually, the family varies widely in composition and so-called "stainless" behavior. The main alloying element is chromium, with nickel added to many grades. Three basic types exist: martensitic, which is hard and wear resistant; ferritic, which is inexpensive and easily formed; and austenitic, which possess the best corrosion resistance and toughness.

TABLE 5

CONSUMPTION OF VANADIUM BY END PRODUCT--
TOOL AND STAINLESS STEELS AND SPECIAL ALLOYS
(Pounds)

	<u>1967</u>	<u>1968</u>
High Speed Steel	955,700	757,000
Hot Work Tool Steel	184,200	152,100
Other Tool Steel	326,600	256,600
Stainless Steel	73,500	96,400
Hard Facing Alloys and Welding Rods	24,000	24,000
Magnetic Alloys	8,000	12,000
High Temperature Alloys	86,000	128,000
Cast Cutting and Wear Resistant Alloys	26,000	32,000

Source: U. S. Bureau of Mines. Not all consumption for these products is shown due to unspecified listings in Bureau of Mines data which are not broken down.

The only commercially-significant stainless steel containing vanadium is Type 422, which has 0.3% vanadium. It is a 12% chromium steel that is hardened to martensite and then tempered at 1200-1300^oF to provide a very stable ferrite-carbide microstructure. This alloy is used in steam power generators as turbine blades, rotors, fasteners, and casing, and in aircraft gas turbines as compressor parts. It is less expensive than the nickel high-temperature alloys, and has advantages in damping characteristics and fabrication; however, the operating temperature capability is lower. The vanadium addition to this alloy plays a role in stabilizing certain microstructural phases and improving temper resistance.

Type 422 alloy accounts for only a small portion of the fifty tons of vanadium reportedly used in stainless steels in 1968.* Another portion could be assigned to the alloy A-286, which many companies report under stainless steel rather than as a high-temperature alloy. Even if both of these are included, there is still a lack of reconciliation between reported vanadium and the uses in stainless steel that is not identifiable.

C. Vanadium in Hard-Facing Alloys and Welding Rods

Hard facing is a specialized process consisting of covering a particular area or an entire surface with a composition more resistant to wear. This is done by depositing molten alloy on the surface in an operation similar to that of welding. The products are particularly effective where lubrication is not possible, as in oil well drilling, ore mining, earth moving, and where economic and operational factors necessitate the use of inexpensive, tough materials that must have this type of protection from abrasive wear.

The hard-facing alloys are generally proprietary and vary widely in composition from lightly alloyed steels to nickel- and cobalt-base alloys. Vanadium is present in amounts from 0.5% to 2.5% in a number of grades containing 12 to 25% total alloy content in an iron base, in many cases paralleling its use in

*AISI statistics do not list grade 422 separately, but include it under "all other."

tool steels. Interestingly, despite the known hardness of vanadium-carbide, most hard-facing alloys seem to develop their great wear resistance from chromium and tungsten. Typically, the higher grade iron-base alloys contain 15-30% chromium, 8-15% tungsten, and no vanadium; and the nickel-cobalt materials are also not alloyed with vanadium.

Vanadium is used in the production of welding wire of certain compositions. One type, containing nickel-manganese-molybdenum, is used in welding the 100-130 ksi alloy steels. A second, a chromium-molybdenum type, is used in welding medium carbon, low-alloy steels heat-treated to 150-240 ksi. The vanadium is added to match the composition of the base metal and not to produce a fine grain size or any special properties in the weldment.

D. Vanadium in Cobalt-Base and Nickel-Base Alloys

1. Magnetic Alloys

Two vanadium-bearing permanent magnetic alloys have been developed by Bell Laboratories, having tradenames of Vicalloy I and Vicalloy II. These iron-cobalt materials contain 10-15% vanadium and are used in computers where very high field strengths are required from small components. Several magnetically "soft" magnet materials, those whose magnetism is induced by electrical current, contain vanadium. In the 2% vanadium Permendur and Supermendur materials, the vanadium makes possible the use of these iron-cobalt alloys which have superior magnetic properties but were unusable due to poor workability and electrical resistivity. These expensive, high-quality magnets are used in receiver diaphragms, very specialized small power transformers (radar and radio), and where corrosion resistance is required.

The actual production of vanadium-containing magnetic alloys is quite small, and represents only a minor amount of the total vanadium consumption.

2. High-Temperature Alloys

The high-temperature alloys are designed for structural service at temperatures of 700^oF and up to 1800^oF; for example, in the hot sections of aircraft gas turbine engines. They are principally alloys of nickel or cobalt with chromium added for oxidation resistance and other elements added for solid solution strengthening and also for precipitation from solid solution. Strength, resistance to creep, and resistance to scaling are required.

The original high-temperature gas turbine alloys were specialized austenitic stainless steels, A-286 and V-57, containing 0.3 to 0.6% vanadium. However, most modern high-temperature alloys do not contain vanadium, as it has a tendency to promote sigma phase formation which is embrittling, and adds little or nothing to the strength or stability of the alloys. Exceptions to this are IN-100 (1% vanadium), a cast alloy for turbine blades, and Hastelloy W (0.6% vanadium), which is a wrought alloy used in gas turbines and for welding dissimilar nickel-base alloys. Hastelloy B-282 (2.0% vanadium) and Hastelloy C-276 (.35% vanadium max) are examples of nickel-molybdenum and nickel-molybdenum-chromium alloys developed for high-temperature strength and resistance to corrosive media. The main applications are in the chemical industry--in the manufacturing of various acids and salts.

3. Cast-Cutting and Wear-Resistant Alloys

A number of cobalt-chromium alloys have been developed for tooling applications. These alloys cannot be hot-worked practically, so are used exclusively as castings. Normally, the compositions used in cutting contain 38 to 40% cobalt, 25 to 32% chromium, 10 to 20% tungsten, 2 to 2.5% carbon. One alloy in the group contains vanadium, that being 3%. The castings are supplied in very nearly-finished tool form, at Rockwell C 60-64, and require only minor grinding before use. While weaker and more brittle than high-speed steel, they show much better heat resistance and are used in single point turning, such as

lathe operations on large castings or forgings, where cooling is impractical. They fill the gap between high-speed steel and cemented carbides, intermediate in both heat resistance and toughness.

The cast, wear-resistant alloy manufacturers, who also frequently are the producers of the hard-facing alloys, see no significant change in the pattern of vanadium consumption in the next ten years.

E. Vanadium in Engineering Alloy Steels

This category of steels is variously called "Alloy Steels," "Machinery Steels," "Heat Treating Steels," or "High-Temperature Steels." Principal users are in automotive parts (bolts, springs, engine valves), steam pipes and headers, and rotors.

Vanadium is present in these steels at levels between 0.2 and 0.4% with the majority of the cases involving a nominal level of 0.25%. Other alloying elements such as chromium, molybdenum, and nickel are used in combination with vanadium. Here, vanadium functions to increase elevated temperature strength through the formation of stable carbides, nitrides, or carbonitrides, and to control the grain-size, thereby making these steels easier to heat-treat.

To achieve the properties of steels bearing vanadium, substitutes containing suitably balanced amounts of chromium, molybdenum, and nickel could be used with modified heat treating schedules. However, this alternative would involve higher costs.

According to an analysis of American Iron & Steel Institute statistics, the trends in Table 6 have been established for consumption of vanadium as a component of engineering alloy steels over the past seven years.

Based on the anticipated growth in demand for these steels, a major United States supplier of vanadium estimates the trends through 1974 to be those tabulated in Table 7.

TABLE 6*
ENGINEERING ALLOY STEELS

Year	Production (Thousands of Ingot Tons)			Vanadium Consumed (Thousands of Pounds)
	Cr-V Steels	Ni-Cr-Mo-V Steels	Cr-Mo-V Steels	
1962	61.4	62.5	89.8	427
1963	69.3	123.3	156.5	698
1964	78.3	137.5	167.2	766
1965	88.8	105.7	208.6	806
1966	83.0	188.2	209.2	961
1967	75.3	159.3	159.5	788
1968	85.6	169.7	169.7	850

* Note: These data are from the annual reports of the American Iron and Steel Institute

TABLE 7

PROJECTED PRODUCTION OF ENGINEERING ALLOY STEELS

<u>Year</u>	<u>Estimated Engineering Alloy Steel Production (Thousands of Tons)</u>	<u>Vanadium Required (Thousands of Pounds)</u>
1969	495	990
1970	520	1,040
1971	540	1,080
1972	570	1,140
1973	590	1,180
1974	610	1,220

F. Vanadium in High-Strength Low-Alloy (HSLA) Steels

The HSLA steels are essentially plain-carbon or low-alloy steels (nominal carbon content of 0.18 to 0.2%) with vanadium or vanadium and columbium at nominal levels of 0.1%. Specific uses are conveniently considered in two categories: (1) constructional steels for such applications as heavy duty equipment, bridges, towers, and buildings; and (2) line pipe for cross-country transmission of high-pressure gas (e.g., welded pipe - 38 inch OD. by 3/8 inch wall thickness and fabricated in 40-ft lengths).

The role of vanadium in HSLA steels is to increase the yield point from about 35,000 psi to the range of 50-65,000 psi. The increase in strength is effected by precipitation of vanadium carbonitrides on normal cooling from warm-working temperatures. The amount of vanadium used and the techniques employed are such that other important properties of the steels, particularly ductility and weldability, are not adversely affected.

Columbium can be considered as a prime substitute for vanadium in HSLA steels. The kinetics of the precipitation or aging reaction involving columbium carbonitrides are such that rapid cooling techniques or cold-finishing, or both, must be used in order to achieve the desired increase in strength. In thicker sections, this may not be practicable and, in any case, involves extra cost. Another alternative which has been suggested is the addition of proper proportions of molybdenum, nickel, and chromium followed by special heat treatments. This alternative also entails higher costs.

Using an analysis of statistics provided by the Bureau of Mines and the American Iron and Steel Institute, the total production of HSLA steels for the period 1963 to 1968, along with estimates of the vanadium and columbium used in these steels, is given in Table 8.

TABLE 8
PRODUCTION OF HIGH-STRENGTH LOW-ALLOY STEELS

<u>Year</u>	<u>Production of HSLA Steels (Thousands of Ingot Tons)</u>	<u>Alloying Elements Consumed (Thousands of Pounds)</u>	
		<u>Vanadium</u>	<u>Columbium</u>
1963	1,680	2,900	560
1964	2,080	4,100	740
1965	2,750	6,100	1,240
1966	3,010	6,670	1,540
1967	3,120	6,280	2,060
1968	3,810	7,230	1,700

From Data of the U.S. Bureau of Mines and the American Iron and Steel Institute

A reasonably valid estimate of the relative amounts of HSLA steels used for constructional and for line pipe applications during the last five years can be obtained through an analysis of shipments reported by AISI as shown in Table 9.

A study of current trends in the steel industry indicates a rapid growth in demand for HSLA steels, particularly for larger diameter and heavier walled line pipe. Estimates of this growth through 1974 provided by a major United States supplier of vanadium are shown in Table 10.

G. Vanadium as a Deoxidant in Continuous Casting of Slabs

In 1969, continuous slab casters in operation in the U.S. have a capacity of 3 million tons of steel with a probable production volume of 1.7 million tons. These casters can produce slabs 6" to 14" thick and 40" to 80" wide. Aluminum is being used as a deoxidant in slab casting, but the formation of alumina during use can cause surface imperfections and nozzle clogging of the tundish (caster feed pot). In addition, the use of aluminum produces only a non-aging steel but the steelmakers would prefer to produce rimmed steels also, with the premium price reserved for the non-aging grades.

Vanadium or mixtures of vanadium and aluminum can be used to deoxidize steel. An extra bonus in the use of vanadium is the strengthening of the slab to reduce or eliminate slab breakage during casting. It is possible that as much as 2.5 million pounds of V would be used in 1974 to continuously cast 11.4 million tons of slabs. (See Table 11.)

Another alternative to the use of vanadium is the addition of a mixture of aluminum and silicon to produce rimmed or drawing quality steel.

H. Vanadium as a Grain Refiner in the Continuous Casting of Billets

The grain size of forging quality steels will generally be fine. Aluminum has been used to inhibit grain growth. However, columbium or vanadium have been substituted for aluminum when stringers of alumina in the cast metal can not be tolerated and to avert clogging of the tundish nozzle through

TABLE 9
LINE PIPE PORTION OF HSLA STEEL PRODUCTION

Year	Shipments of HSLA Steels (Thousands of Tons)		Percent of Total Shipments as Line Pipe
	Total	Line Pipe	
1964	1,832	493	26.8
1965	2,376	697	29.4
1966	2,596	997	38.4
1967	2,439	931	38.1
1968	2,923	1,129	38.4

From Data of the American Iron and Steel Institute

TABLE 10
PROJECTED PRODUCTION OF HIGH STRENGTH LOW ALLOY STEELS

<u>Year</u>	<u>Production of HSLA Steels</u> <u>(Thousands of Ingot Tons)</u>			<u>Alloying Elements</u> <u>Consumed</u> <u>(Thousands of Pounds)</u>	
	<u>Total</u>	<u>Line Pipe</u>	<u>Construc-</u> <u>tional</u>	<u>Vanadium</u>	<u>Columbium</u>
1969	3,700	1,800	1,900	8,150	1,660
1970	4,000	2,000	2,000	8,800	1,800
1971	4,200	2,100	2,100	9,660	1,680
1972	4,500	2,200	2,300	10,350	1,800
1973	4,700	2,400	2,300	11,280	1,640

TABLE 11

PROJECTED VANADIUM USE IN CONTINUOUSLY CAST STEEL SLABS

<u>Year</u>	<u>Continuously Cast Slabs (millions of tons)</u>	<u>Vanadium Consumed/Yr (millions of pounds)</u>
1969	1.7	0.10
1970	2.6	0.1 - 0.30
1971	3.9	0.2 - 0.60
1972	4.4	0.3 - 0.80
1973	8.5	0.5 - 1.50
1974	11.4	0.8 - 2.50

which hot metal enters the caster. The problem of grain growth can be overcome by forming aluminum nitride with additions of 1.0 to 4.0 lbs./ton of aluminum depending on the steel's oxygen content. Grain growth can be controlled using 1 to 2 lbs./ton of vanadium, but this is a far more costly procedure. However, vanadium increases yield strength, increases resistance to hot-tearing, and provides a cleaner steel surface. On the debit side, impact strength is reduced somewhat, and a higher yield point makes bending more difficult. An estimate of future consumption in the face of vanadium's mixed value-in-use is difficult to forecast. For this reason a range of consumption is shown in Table 12 with the lower value being the minimum expected use and the higher value the maximum expected use.

I. Vanadium in Alloy Cast Irons

In 1969, it is estimated that about 2.3 million tons of alloy cast iron will be produced rising to about 3 million tons in 1974.

The common alloying elements in cast iron are chromium, copper, molybdenum, nickel, and vanadium. Vanadium is most often used in combination with other alloying ingredients, usually in amounts between 0.08% and 0.2% (see Table 13).

Vanadium is the principal element used for increasing tensile strength and hardness. V, along with Mo and Cr, also improves the elevated temperature properties, wear resistance and heat-treatment hardenability characteristics of castings. V, when used along with Mo, produces finer, more uniform graphite flakes. Chromium, molybdenum, and nickel exert a synergistic effect on vanadium resulting in a decrease in the total amount of alloying ingredients needed to do the job. Table 14 is a chart showing the replacement options open for various V alloys.

The alloy to be used would be dictated mostly by cost considerations.

TABLE 12

PROJECTED CONSUMPTION OF VANADIUM IN BILLET CASTING

<u>Year</u>	<u>Vanadium Consumed in Billet Casting</u> <u>(millions of pounds/year)</u>
1969	0.1 - 0.2
1970	0.1 - 0.5
1971	0.2 - 0.8
1972	0.3 - 1.2
1973	0.3 - 2.0
1974	0.5 - 5.0

TABLE 13
USE OF VANADIUM IN CAST IRON (1969)

<u>Alloying Metals</u>	<u>Total Qty Produced 000 tons</u>	<u>Total V Consumed 000 lbs</u>	<u>Alloy Function</u>
V	25	50	High strength applications
Ni-V	10	20	High strength applications
Cu-V	15	30	Auto and machine tool parts
Cu-Cr-V	15	30	High strength applications
Ni-Cr-V	15	30	Auto manifolds
Mo-V	50	100	Cam shafts
Cr-V	50	100	Elevated temperature applications
Cr-Mo-V	125	<u>300</u>	Heavy duty brake drums, cam shafts
	TOTAL	<u>660</u>	

TABLE 14

REPLACEMENT OPTIONS FOR VANADIUM IN CAST IRON

<u>Alloying Element(s)</u>	<u>Replacement</u>
V	Mo
Ni-V	Cu-Mo
Cu-V	Cu-Mo
Cu-Cr-V	Cu-Cr-Mo, Ni-Cr-Mo, Cr-Mo
Ni-Cr-V	Ni-Cr-Mo, Cu-Cr-Mo
Mo-V	Cu-Mo, Ni-Cu-Mo, Mo-Cr
Cr-V	Cr-Mo, Ni-Cr-Mo, Cu-Cr-Mo
Cr-Mo-V	Ni-Cr-Mo

It is expected that the demand for vanadium in alloy cast irons will increase at a yearly rate of about 8% to meet the demand for fabricated parts with a higher strength to weight ratio. In 1974 demand for vanadium for alloy cast iron applications should reach almost 1,000,000 lbs. (see Table 13).

J. Vanadium in Titanium Alloys

Vanadium is a strong beta stabilizer in titanium, and as such promotes good hot and cold workability. As a beta stabilizer, it provides the very important ability of alpha-beta titanium alloys to be strengthened by heat treatment. Strengthening heat treatments in titanium alloys are based on the transformation of the beta phase to the alpha phase either by nucleation and growth at slow cooling rates, or by martensitic-type shear at fast cooling rates.

Titanium alloys are generally classified as (1) alpha or super-alpha, (2) alpha-beta, and (3) beta. This classification can also be used to describe the basic areas of titanium alloy applications and development. The alpha alloys, typified by Ti-5Al-2.5Sn, are generally used where heat-treatable strengths are not required, but some improvement over unalloyed titanium is necessary. Super-alpha alloys have been developed for applications requiring high creep resistance and good thermal stability, but only low temperature moderate strength. Examples of these alloys are Ti-8Al-1Mo-1V, Ti-6Al-2Sn-4Zr-2Mo, and Ti-5Al-6Sn-2Zr-1Mo-1/4Si. The super alpha alloys usually contain a small amount of beta isomorphous elements, molybdenum and vanadium, for strengthening and workability. Alpha-beta alloys, such as Ti-6Al-4V and Ti-5.5Al-5.5V-.7Fe-.7Cu ("662") cover a broad range of applications, but generally are utilized in applications requiring high strength, good toughness, and thermal stability up to moderate temperatures. Beta alloys, such as Ti-13V-11Cr-3Al and Ti-11.5Mo-6Zr-4.5Sn, are generally used in sheet and fastener applications. Extremely high strengths can be obtained after solution treating and aging. The high strengths are maintained to moderate temperatures. The beta alloys exhibit high ductility and formability in the solution-treated, or all-beta, state.

TABLE 15
FORECAST DEMAND FOR VANADIUM
IN ALLOY CAST IRON

Year	Demand, 000 pounds of V
1969	660
1970	710
1971	765
1972	825
1973	890
1974	960

Beta-isomorphous alloying elements, that is, those elements having the same crystal structure as the high-temperature (beta) phase of titanium, are used in all three alloy classifications described. The elements which form this type system with titanium are vanadium, molybdenum, tantalum, and columbium. Of these, vanadium has been the most widely used, although there is a growing use of molybdenum, especially in the super-alpha type. Although vanadium is not quite as strong a beta stabilizer as molybdenum, it does have certain advantages over the other three elements. These are (1) fewer segregation problems because of its lower melting temperature, (2) lower density, (3) cost-availability, and (4) stronger beta stabilizing power than tantalum and columbium.

Vanadium is added to titanium as a master alloy which is produced by aluminothermic reaction. The two most popular master alloys are 60Al-40V, which is used primarily for Ti-6Al-4V, and 15Al-85V, which is used where the vanadium content in the titanium alloy is equal to or greater than the aluminum. The National Stockpile Purchase Specification P-58-R for vanadium oxide is satisfactory for use in all current alloys. Should requirements change, upgrading could be performed readily.

The future demand for vanadium in the titanium alloys depends then not only on the bulk market for titanium, but specifically on the areas in which significant alloying of vanadium will occur. For example, the titanium market for use in chemical process equipment is expected to expand rapidly in the next decade, but this market will consist largely of either pure titanium or of the Ti-0.2Pd alloy. Therefore, vanadium demand will not be increased by this market segment.

The National Materials Advisory Board of the National Academy of Sciences/National Academy of Engineering has recently issued a document entitled, "Usage of Titanium and Its Compounds with Comments on Scrap and Sponge," (MAB-249 which is subject to special export controls) in which the effort is made to define the titanium market through 1978.

Analysis of this report leads to the following summaries:

- 1. Titanium consumption rate is expected to quadruple between 1968 and 1978.**
- 2. Most of this expansion will occur in the aerospace field with all other applications amounting to less than 10 percent of the total.**
- 3. Many recently-developed alloys will replace to a certain extent the two major alloys, Ti-6Al-4V and Ti-5Al-2.5Sn. Most of these alloys contain vanadium in percentages varying between one and eight percent. However, one promising alloy, Ti-6Al-2Sn-4AR-2Mo, contains no vanadium.**
- 4. Jet engine applications rely heavily on Ti-5Al-2.5Sn, a non-vanadium alloy. Also, the Ti-6Al-2Sn-4Zr-2Mo alloy is promising to replace some of the Ti-6Al-4V used. Therefore, the use of vanadium in aircraft engine applications will probably lag behind overall titanium increases. A figure of 75% of the titanium expansion is anticipated.**
- 5. Titanium alloys for airframes are based upon high strength at relatively low temperatures. The most common current alloys Ti-6Al-4V and Ti-5.5Al-5.5V-2Sn-.7Fe-.7Cu ("662") probably will be replaced to some extent by other alpha-beta or beta alloys which contain vanadium. Therefore, vanadium usage here is expected to expand at the same rate as titanium, that is, about five times.**
- 6. Approximately one-third of the non-aerospace applications involved the vanadium-bearing alloys indicated in Table 2 of MAB-249. Usage in these applications is expected to triple (See Figure 12 of MAB-249 which is a special export); however, the two largest components of this expansion -- desalination and chemical process equipment -- probably will not utilize vanadium-bearing alloys. Therefore, vanadium usage is expected to only double in this area.**

The 1968 Minerals Yearbook, published by the U. S. Department of Interior, Bureau of Mines, reported a 1967 consumption of 614 short tons consisting primarily of vanadium contained in vanadium-aluminum alloy use in

making titanium alloys. Assuming that this was all used in making Ti-6Al-4V, a total of 27.4×10^6 pounds of alloy titanium would be involved. This figure is comparable to the 27×10^6 total titanium estimated in MAB 249. If we assume that this quantity was used for titanium alloys and that it was used uniformly through the product mix described on page 1 of MAB-249, the 1967 usages shown in Figure 1 are obtained. The curves for the time period through 1978 are obtained by incorporating the estimates obtained in the paragraphs above. A total demand of 3.3 million pounds per year is anticipated for 1978.

Alternate materials to vanadium as an alloy constituent are readily available. Substitution with molybdenum is already a fact in some alloys, and the slight alteration of design criteria necessary to make such changes could be readily achieved if a compelling reason should arise.

K. Vanadium and Vanadium-Base Alloys

By far, the principal potential application for alloys based on vanadium is in the nuclear industry as fuel cladding for advanced liquid-metal cooled fast-breeder reactors. Vanadium-base alloys are now considered a major backup for austenitic stainless steels for this application.

Nominal compositions of some alloys currently included in development programs sponsored by the Atomic Energy Commission are listed in Table 16.

Vanadium is an attractive base for fast-breeder reactor cladding alloys because of its favorable nuclear characteristics (low neutron absorption cross section in the 30 to 300 key range), higher creep strength, and possibly greater resistance to fast-neutron-induced damage relative to the stainless steels. Recent data indicate, however, that the corrosion resistance of the vanadium alloys which have been studied may be less than satisfactory in flowing sodium. This behavior is due primarily to the effects of oxygen in the sodium, which, depending upon the alloy, the temperature, and the oxygen content under consideration, results in surface oxidation with attendant spalling, embrittlement

FIGURE 1
Vanadium Usage in Titanium Alloys
(Cumulative)

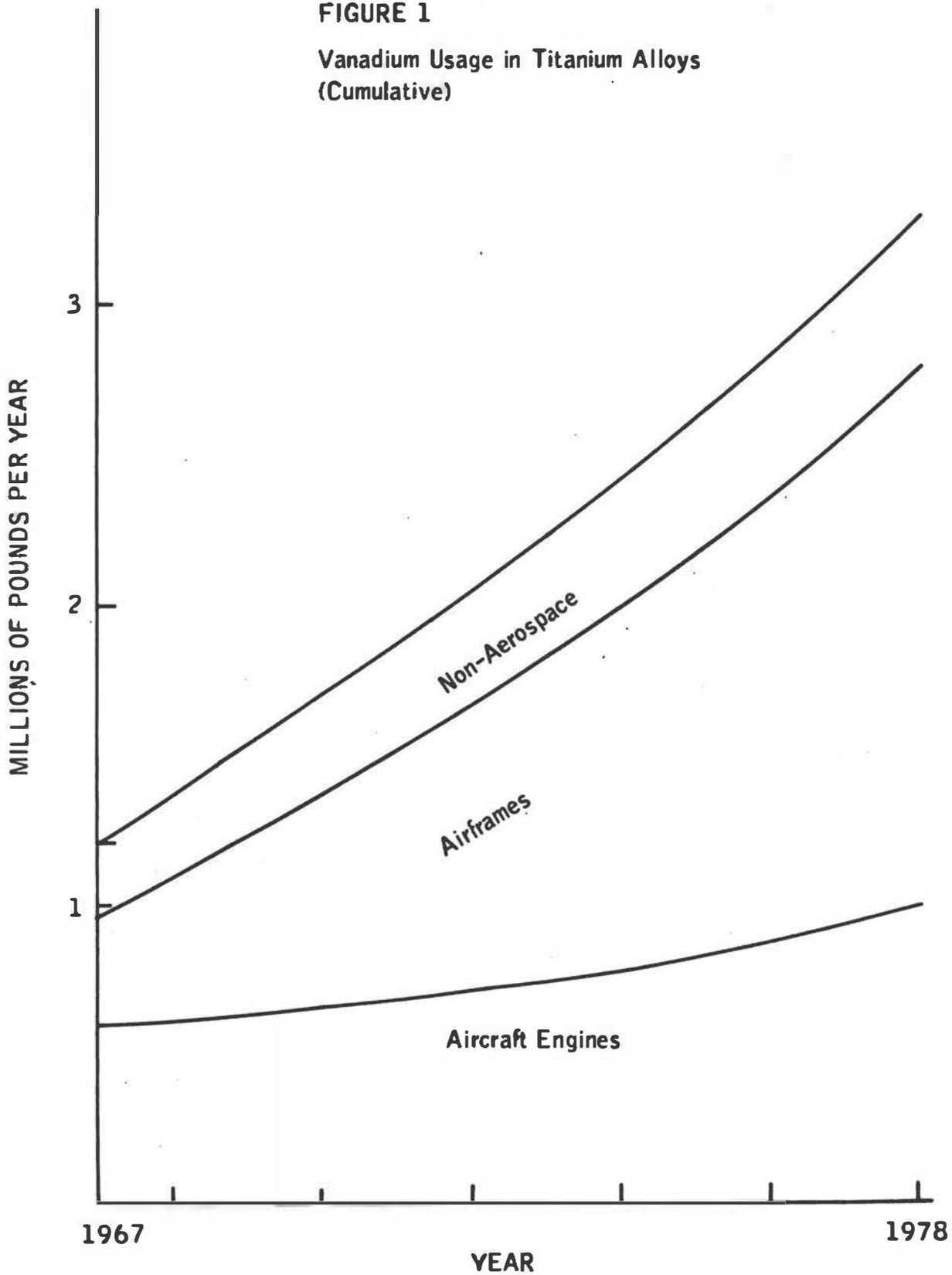


TABLE 16

NOMINAL COMPOSITIONS (WT %) OF CANDIDATE FUEL-CLADDING ALLOYS

<u>V</u>	<u>Ti</u>	<u>Cr</u>	<u>Fe</u>	<u>Ta</u>	<u>Nb</u>	<u>Zr</u>	<u>C</u>
80	20						
78.5	15	7.5					
80	5	15					
90		10					
86.5		9	3			1.3	0.05
80.5		8		10		1.3	0.05
87.5			6		5	1.3	0.05

of the alloy, internal oxidation, or combinations of these effects. Alloy development and further evaluation are in progress to improve this situation.

Molybdenum- and cobalt-base alloys are currently under consideration as alternative fast-reactor fuel cladding back-ups for stainless steels. They exhibit excellent resistance to corrosion by sodium but from the nuclear standpoint are not as attractive as vanadium alloys. Fabricability and radiation damage constitute major problem areas.

The present demand for vanadium alloys is limited to experimental quantities of sheet, round bar, and small-diameter, thin-wall tubing.

Proper industrial technology will have to be established before vanadium alloy tubing can come into its own as a major item for use as fuel cladding in a viable fast-breeder reactor economy. Estimates for the future demand of vanadium alloys for such tubing usually begin at the year 1985. Depending upon the assumptions used, the demand in the period 1985 to 2000 could be very high, ranging between 40 and 60 million pounds for this 15-year period.

The assumptions used in arriving at these figures are listed below.

1. The growth of nuclear electric generating capacity will follow the the estimates presented in the document, "Estimated Growth of Civilian Nuclear Power," USAEC Division of Operations Analysis and Forecasting, WASH-1055 (March 1965).
2. All nuclear capacity from 1985 to 2000 will be Liquid Metal Fast-Breeder Reactors (LMFBR's).
3. All LMFBR's will be 1000 Mw (e) facilities and will conform to one of the two designs presented in the document, "Comparison of Two Sodium Cooled 1000 Mw(e) Fast Reactor Concepts," General Electric Task I Report - LMFBR Follow-On Study, GEAP-5618.

Both a "conservative" and an "advanced" design are described in this report.

4. An alloy of the composition shown as fifth in the tabulation presented under "Specific Uses" above (86.5% vanadium) will be used for core cladding, and stainless steel containing no vanadium will be used for the radial blanket cladding.

Based on these assumptions, the demand for vanadium for the three five-year periods between 1985 and 2000 will be as in Table 17.

In view of the contingencies cited in the discussions above, the real future demands for vanadium for the nuclear applications under consideration are recognized to lie anywhere between zero and the figures given in this table.

L. Vanadium in Columbium and Tantalum Alloys

1. Wrought Product

Several columbium- and tantalum-based alloys have been developed in recent years utilizing vanadium as an alloy constituent. The most prominent of these are Ta-30Cb-8V and Cb-5Mo-5V-1Zr. The alloy Ta-30Cb-8V ("TCV") was chosen by the Air Force in the early 1960's as the tantalum alloy for several manufacturing methods development programs based upon a combination of properties, including weldability and coatability. However, alloys with superior combinations of properties exist today, and "TCV" is not receiving significant attention at this time.

Based upon these data, an alloy containing significant amounts of vanadium is not likely to be developed during the next decade.

2. Coating and Brazing

In order to withstand the high temperatures at which they have superior mechanical properties, all refractory metals developed to date have to be coated prior to use in an oxidizing atmosphere.

TABLE 17
PROJECTED DEMAND FOR VANADIUM FOR
NUCLEAR POWER REACTOR APPLICATIONS

Period	Vanadium Required for Designated Period (millions of pounds)	
	Advanced LMFBR Design	Conservative LMFBR Design
1985-1990	9	13
1990-1995	13	20
1995-2000	<u>18</u>	<u>27</u>
TOTAL	<u>40</u>	<u>60</u>

Two basic types of coatings for refractory metals have been developed--aluminide and silicide. Some investigators have indicated that vanadium modifiers to silicide coatings improve the performance. Since the effectiveness of the elemental additions to the silicide is somewhat dependent on the substrate being coated, there is a potential for vanadium as a modifier in silicide coatings for specific substrates. Several coating compositions currently under consideration are shown in Table 18. The technology of refractory metal coatings is not well advanced at this stage, and the future course is difficult to predict. Possibly, greater than 500,000 pounds of columbium-base alloys could be in development or use for the hottest stages of gas turbine and supersonic engines in 1978. Assuming that one of the vanadium-bearing silicide coatings was chosen for coating the components, about 10,000 pounds of coating material, containing between 500 and 2000 pounds of vanadium, would be required.

Reportedly, one brazing alloy, Cb-65%V, has been used for joining of tantalum alloy components. Since most columbium and tantalum alloys are selected for high temperatures, brazing is not expected to be used extensively in components fabricated from these alloys.

3. Summary

Because of the indefinite future of columbium and tantalum alloys and the even more questionable participation of vanadium for either alloy constituent, braze component, or coating components, it is difficult to predict vanadium demand. In any event, it is difficult to envision the need arising for more than tens of thousands of pounds per year by 1978, and this is a very small quantity relative to the requirements in other applications, such as steel and titanium.

M. Vanadium in the Chemical Industry

Vanadium in the form of specific compounds, for the most part inorganic, continues to perform almost uniquely in a number of specific areas of chemistry but none of more importance than that of catalysis. These commercial

TABLE 18
EXPERIMENTAL COATING MATERIAL FOR REFRACTORY METALS

Composition	Data Source
Si-20Cr-5V Si-20Cr-5Ti-10VSi ₂ Si-20Cr-5Ti-10Fe-10VSi ₂	"Development of Slurry Coatings for Tantalum, Columbium, and Molybdenum Alloys," by S. Priceman and L. Sama, Sycor Division, Sylvania Electric Products, Inc., AFML-TR-65-204, September 1965.
(35Mo-35W-15Ti-15V)Si ₂	"Slurry Applied Duplex Coatings for Tantalum and Columbium Alloys" by A. R. Stetson and R. T. Wimber, Solar Division, International Harvester Company, RDR-1471.

scale synthetic operations vary from old and exceedingly well-established inorganic chemistry to new and ever-growing uses which, for the most, embody organo-chemical manipulations in the hydrocarbon monomer and polymer field. Three specific areas (a) the synthesis of H_2SO_4 , (b) the oxidation of hydrocarbons, and (c) the polymerization of mono- and di-olefins presently consume the bulk of vanadium. However, research reports continue to emphasize the utility of vanadium-based compounds in chemistry, but no major new uses than those delineated are foreseen in the next few years. In most instances, the critical nature of the use is recorded and commercially useful alternates are identified where possible. The chemical industry reportedly used 132 short tons of vanadium in 1967. This use is expected to increase gradually to 200-250 short tons by 1975. However, inasmuch as consumption statistics for the chemical industry are more difficult to obtain than those for the metallurgical industry, conceivably the 1967 consumption figure and the increase in consumption projected for 1975 could be from 10 to 20 percent higher than these stated figures.

1. Manufacture of Sulfuric Acid

The oxidation of sulfur dioxide (SO_2) to sulfur trioxide (SO_3) is by far the most important vapor phase oxidation reaction known. The economic climate of the U.S. chemical industry is intimately tied to the production and consumption of sulfuric acid. Research and development in this field have established beyond question the preference for vanadium-based catalysts as judged by (a) longer life (b) higher average efficiency (c) immunity to poisoning by arsenic, chlorine, etc., (d) greater physical ruggedness and greater availability versus its sole competitor, namely, those catalysts based on platinum. The use of slightly lower SO_2 concentrations (6-8%) in the process stream versus 10% for platinum-based catalytic units and the lack of salvage value for the spent catalyst have done little to change the picture. No major changes in process are visualized for the foreseeable future, but a continuing increase in the use of this basic commodity, sulfuric acid, is forecast (Table 19) to keep pace with the country's growth.

TABLE 19
SULFURIC ACID PRODUCTION

Year	Thousands of Short Tons*
1965	24,790
1966	28,477
1967	28,197
1968	28,382
1969	34,200 - 34,500 Forecast

* (1) Survey of Current Business, June, 1969, Number 6.

(2) C & E News, September 2, 1968.

2. Oxidation of Hydrocarbons

The catalytic oxidation of substances at solid surfaces in the presence of O_2 or air has yielded, in numerous instances, commercially acceptable and even preferred routes to basic chemical intermediates.* The synthesis of maleic anhydride from benzene; phthalic anhydride from naphthalene or ortho xylene; benzoic acid from toluene; anthraquinone from anthracene; diphenyl ketone from fluorene; p-toluic acid and terephthalic acid from p-cymene are representative of this ever growing field. For the most part, catalysts based solely on fused V_2O_5 or V_2O_5 deposited upon, or promoted by, MoO_3 and other oxides, e.g., Al_2O_3 , Ag_2O , SiO_2 or salts, e.g., K_2SO_4 and $K_2S_2O_7$ form the basis for these potent chemical conversions. Vanadium is and will continue to be important in this area of chemistry since no satisfactory replacement is on the horizon based on current published literature.

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- * 1. Marek & Hahn, "The Catalytic Oxidation of Organic Compounds in the Vapor Phase", New York, Chemical Catalog Co., 1932.
2. Emmett, Paul H., Catalysis VII; Rheinhold Publishing Corporation, New York, (1960).
3. Predicasts, Issue #35, First Quarter 1969, April 18, 1969.
4. C & E News, April 7, 1969.
5. Hydrocarbon Processing, November 1968, page 165.
- 5a. Ibid, January, 1969, page 123.
6. Oil Paint and Drug Reporter, March 10, 1969, page 3.

3. Polymerization

a. Hydrocarbons

Research in the field of catalysis based on transition elements and reducing agents, e.g., the metal alkyls were given impetus by the work of Ziegler and others starting in 1949. A great variety of Group IV-VIII transition metal compounds and an equally great variety of compounds derived from Group I-III metals have been found useful. Not all compounds and not all combinations are equally effective in giving a desired result, however. For the most part, the agents that are preferred for the polymerizations of ethylene and the stereo specific polymerization of other α -olefins, e.g., propylene, are generally heterogeneous and based on titanium rather than vanadium. Probably, this preference will continue for the immediate future for technical as well as economic reasons.

In two important and growing areas of polymerization, however, catalytic systems based on vanadium appear again to be somewhat unique. For example, in the polymerization of C_4 - C_5 diene hydrocarbons, structural regularity is conferred almost exclusively as shown in Table 20. The accessibility of these tough Balata-like polymers from readily available raw materials will prompt their broad scale evaluation as elasto plastics.

A similar and even more rigidly defined specificity exists in the synthesis of amorphous or rubbery EPM copolymers derived from ethylene/propylene and EPDM copolymers synthesized from ethylene, a suitable α -olefin such as propylene and a non-conjugated diene. These EPDM polymers are growing at the rate of $\sim 30\%$ per year, and, based on reliable forecasts, will probably reach a production level in this country of 5-600,000,000 pounds by 1975. Three vanadium based catalyst components, namely $VOCl_3$, VCl_4 and $V(AA)_3$, are being used. Based on these projections, additional vanadium demand of 100-150 short tons are visualized by 1975 by the chemical industry for this use,

TABLE 20
MICROSTRUCTURE OF POLYDIENES*

Catalyst	Polybutadiene		1,2	Polyisoprene		
	1,4-trans	1,4-cis		1,4-trans	1,4-cis	1,2&3,4
$AlEt_2Cl/VCl_3$	95-87		3-5			
AlR_3/VCl_4	95		5			
AlR_3/VCl_3	99		1	99-100		
$AlR_3/V(AA)_3^{**}$	12-13		78-86			90
$AlR_3/TiCl_4$						
Al/Ti <1	6	91	3	96	--	4
Al/Ti >1	21-57	31-69	2-11	--	95	5

- * 1. Natta, G., et al, *Chim. Ind. (Milan)*, 40, 362 (1958).
 2. Belgian Patent, 543,292 (Goodrich-Gulf Chemicals, Inc.) 1955.
 3. Wilke, G. *Angew., Chem.*, 68, 306 (1956).
 4. Natta, G., et al, *Chim. Ind. (Milan)*, 41, 398 (1959).
 5. Gaylord & Mark, "Linear & Stereo Regular Addition Polymers"; Interscience Publishers, Inc., New York, (1959).
 6. Reich & Schindler, "Polymerization by Organo Metallic Compounds," Interscience Publishers, Inc., New York, (1966).
 7. Chemical Week, June 28, 1969.

** AA = acetyl acetone.

assuming no improvement in catalyst productivity or the discovery of a suitable alternate.

4. Ceramics *

The use of vanadium in the ceramics industry is exceedingly limited and shows little if any sign of potential growth. Small amounts, probably less than 5000 pounds/year, of V_2O_5 are consumed by the chemical industry in the production of a yellow stain for coloring pottery and glass. Alternates are available which are better technically, but considerably more expensive.

V. SUITABILITY OF STOCKPILE SPECIFICATION

The present stockpile of vanadium pentoxide (V_2O_5) does not restrict the content of deleterious elements such as nitrogen and boron. Accordingly, it may be unsuitable for the production of vanadium metal, if a significant need develops for vanadium in the nuclear reactor area. It is recommended that the following chemistry be specified for vanadium pentoxide for conversion to reactor grade material, if the need arises:

V_2O_5 - 99.9% min	Mo - 0.02% max
C - 0.01% max	B - 0.005% max
SiO_2 - 0.017% max	W - 0.02% max
N - 0.01% max	

In specification P-58-R dated December 11, 1957, it is suggested that the title of the specification be changed from "Vanadium" to "High Purity Vanadium Pentoxide" or "C. P. Vanadium Pentoxide."

*Private Communication: The Ceramic Color and Chemical Corporation, New Brighton, Pa.

Unclassified

Security Classification

DOCUMENT CONTROL DATA - R & D		
<i>(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)</i>		
1. ORIGINATING ACTIVITY (Corporate author) National Materials Advisory Board, Committee on Critical and Strategic Materials, Panel on Vanadium		2a. REPORT SECURITY CLASSIFICATION Unclassified
		2b. GROUP
3. REPORT TITLE TRENDS IN THE USE OF VANADIUM		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Report of the Panel on Vanadium--June 1969-March 1970		
5. AUTHOR(S) (First name, middle initial, last name) NMAB Panel on Vanadium		
6. REPORT DATE March 1970	7a. TOTAL NO. OF PAGES 55	7b. NO. OF REFS 22
8a. CONTRACT OR GRANT NO. GS+OO-(P) 94008	8b. ORIGINATOR'S REPORT NUMBER(S) NMAB-267	
8c. PROJECT NO.		
8d.		
9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)		
10. DISTRIBUTION STATEMENT		
11. SUPPLEMENTARY NOTES		12.
13. ABSTRACT <p>The major source of vanadium in the future appears to be vanadium-bearing magnetite ores from which vanadium will be co-produced during steel manufacturing. The growth areas for vanadium in the steel industry are in high-strength, low alloy steels (HSLA) and in possibly continuous casting of steel slabs and billets. The demand for vanadium in these steels is predicted to exceed all other cumulative uses of vanadium—with HSLA steels making the biggest demand. In the face of a substantial price rise or of a shortage in vanadium, columbium could be substituted in steels. The requirements for vanadium in titanium alloys will be proportional to the growth of the titanium industry. As yet, the choice has not been made between stainless steels and vanadium alloys as a fuel element cladding in fast breeder nuclear reactors. If vanadium alloys become the more desirable cladding, the increase in demand will not be felt for approximately fifteen years.</p>		

Unclassified

Security Classification

