VANADIUM AND VANADIUM ALLOYS

1. Introduction

Vanadium [7440-62-2], V, (at. no. 23, at. wt 50.942) is a member of Group 5 (VB) of the Periodic Table. It is a gray body-centered-cubic metal in the first transition series (electronic configuration $4s^2 3d^3$). When highly pure, it is very soft and dutile. Because of its high melting point, vanadium is referred to as a refractory metal, as are niobium, tantalum, chromium, molybdenum, and tungsten (see REFRACTORIES). The principal use of vanadium is as an alloying addition to iron (qv) and steel (qv), particularly in high strength steels and, to a lesser extent, in tool steels and castings (see TOOL MATERIALS). Vanadium is also an important beta-stabilizer for titanium alloys (see TITANIUM AND TITANIUM ALLOYS). Interest has been shown in the intermetallic compound V_3Ga [12024-15-6] for superconductor applications.

Vanadium was first discovered in 1801 by del Rio while he was examining a lead ore obtained from Zimapan, Mexico. The ore contained a new element and, because of the red color imparted to its salts on heating, it was named erythronium (redness). The identification of the element vanadium did not occur until 1830 when it was isolated from cast iron processed from an ore from mines near Taberg, Sweden. It was given the name vanadium after Vanadis, the Norse goddess of beauty. Shortly after this discovery, vanadium was shown to be identical to the erythronium that del Rio had found several years earlier.

2. Occurrence

Vanadium is widely distributed throughout the earth but in low abundance, ranking 22 among the elements of the earth's crust. The lithosphere contains ca 0.07 wt % vanadium and few deposits contain more than 1–2 wt %. Vanadium occurs in uranium-bearing minerals of Colorado, in the copper, lead, and zinc vanadates of Africa, and with certain phosphatic shales and phosphate rocks in the western United States. It is a constituent of titaniferous magnetites, which are widely distributed with large deposits in Russia, South Africa, Finland, the People's Republic of China, eastern and western United States, and Australia. At one time, the largest and most important vanadium deposits were the sulfide and vanadate ores from the Peruvian Andes, but these are depleted. Most of the vanadium reserves are in deposits in which the vanadium would be a by-product or coproduct with other minerals, including iron, titanium, phosphate, and petroleum.

Trace amounts of vanadium have been found in meteorites and seawater, and it has been identified in the spectrum of many stars including the earth's sun. The occurrence of vanadium in oak and beech trees and some forms of aquatic sea life indicates its biological importance.

There are over 65 known vanadium-bearing minerals, some of the more important are listed in Table 1. Patronite, bravoite, sulvanite, davidite, and roscoelite are classified as primary minerals, whereas all of the others are secondary products which form in the oxidizing zone of the upper lithosphere. The carnotite and roscoelite ores in the sandstones of the Colorado Plateau have been important sources of vanadium as well as of uranium.

The metallic vanadates of lead, copper, and zinc, which occur in Namibia (southwest Africa) and Zambia, are also a large resource of vanadium-bearing ores, as are the phosphatic shales and rocks of the phosphoria formation in Idaho and Wyoming. Vanadium salts are obtained as by-products of the phosphoric acid and fertilizer industries (see FERTILIZERS). Large reserves of vanadium in Arkansas and Canada and the titaniferous magnetite ores will probably become increasingly significant as sources of production. Certain petroleum crude oils, especially those from South America, contain varying amounts of vanadium compounds. These accrue as fly ash or boiler residues upon combustion of the crude oils and they can be reclaimed (see AIR POLLUTION CONTROL METHODS).

3. Properties

3.1. Physical Properties. Vanadium is a soft, ductile metal in pure form, but it is hardened and embrittled by oxygen, nitrogen, carbon, and hydrogen (1,2). Selected metal additions lead to higher strength alloys which maintain a reasonable level of ductility (3). Its thermal conductivity is significantly lower than that of copper. Important physical properties of vanadium are listed in Table 2. Some of these properties depend on the purity of the material used for the determinations. Although a purity level of 99.99% has been achieved experimentally, such high purity material has not been used for all of the determinations listed (7).

3.2. Chemical Properties. Vanadium has oxidation states of +2, +3, +4, and +5. When heated in air at different temperatures, it oxidizes to a brownish black trioxide, a blue-black tetroxide, or a reddish orange pentoxide. It reacts readily with chlorine at fairly low temperatures (180°C) forming VCl_4 and with carbon and nitrogen at high temperatures forming VC and VN, respectively. The pure metal in massive form is relatively inert toward oxygen, nitrogen, and hydrogen at room temperature.

Vanadium is resistant to attack by hydrochloric or dilute sulfuric acid and to alkali solutions. It is also quite resistant to corrosion by seawater but is reactive toward nitric, hydrofluoric, or concentrated sulfuric acids. Galvanic corrosion tests run in simulated seawater indicate that vanadium is anodic with respect to stainless steel and copper but cathodic to aluminum and magnesium. Vanadium exhibits corrosion resistance to liquid metals, eg, bismuth and low oxygen sodium.

3.3. Properties of Alloys. Most of the alloys developed to date were intended for service as fuel cladding and other structural components in liquid-metal-cooled fast-breeder reactors. Alloy selection was based primarily on the following criteria: corrosion resistance in liquid metals, including lithium, sodium, and NaK, and a mixture of sodium and potassium; strength; ductility, including fabricability; and neutron considerations, including low absorption of fast neutrons as well as irradiation embrittlement and dimensional-variation effects. Alloys of greatest interest include V 80, Cr 15, Ti 5 [39308-80-0]; V 80, Ti 20 [12611-15-3]; V 77.5, Ti 15, Cr 7.5 [51880-37-6]; and V 86.65, Cr 9, Fe 3, Zr 1.3, C 0.05 [84215-85-0].

Based on considerations of economics, fabricability, and performance, reasonable allowable levels of interstitial elements are as follows:

Element	Allowable level, ppm wt
carbon	200
nitrogen	100
oxygen	300
hydrogen	100

Because of the effects of impurity content and processing history, the mechanical properties of vanadium and vanadium alloys vary widely. The typical RT properties for pure vanadium and some of its alloys are listed in Table 3. The effects of alloy additions on the mechanical properties of vanadium have been studied and some alloys that exhibit room-temperature tensile strengths of 1.2 GPa (175,000 psi) have strengths of up to ca 1000 MPa (145,000 psi) at 600°C. Beyond this temperature, most alloys lose tensile strength rapidly.

As in the case of many metal–alloy systems, weld ductility is not as good as that of the base metal. Satisfactory welds can be made in vanadium alloys provided the fusion zone and the heat-affected zone (HAZ) are protected from contamination during welding. Satisfactory welds can be made by a variety of weld methods, including electron-beam and tungsten-inert-gas (TIG) methods. It is also likely that satisfactory welds can be made by advanced methods, eg, laser and plasma techniques (see LASERS; PLASMA TECHNOLOGY).

4. Manufacture

4.1. Ore Processing. Vanadium is recovered domestically as a principal mine product, as a coproduct or by-product from uranium–vanadium ores, and from ferrophosphorus as a by-product in the production of elemental phosphorus. In Canada, it is recovered from crude-oil residues and in the Republic of South Africa as a by-product of titaniferous magnetite. Whatever the source, however, the first stage in ore processing is the production of an oxide concentrate.

The principal vanadium-bearing ores are generally crushed, ground, screened, and mixed with a sodium salt, eg, NaCl or Na_2CO_3. This mixture is roasted at ca 850°C and the oxides are converted to water-soluble sodium metavanadate, $NaVO_3$. The vanadium is extracted by leaching with water and precipitates at pH 2–3 as sodium hexavanadate, $Na_4V_6O_{17}$, a red cake, by the addition of sulfuric acid. This is then fused at 700°C to yield a dense black product which is sold as technical-grade vanadium pentoxide. This product contains a minimum of 86 wt % V_2O_5 and a maximum of 6–10 wt % Na_2O.

The red cake can be further purified by dissolving it in an aqueous solution of Na_2CO_3. The iron, aluminum, and silicon impurities precipitate from the solution upon pH adjustment. Ammonium metavanadate then precipitates upon the addition of NH_4Cl and is calcined to give vanadium pentoxide of greater than 99.8% purity.

Vanadium and uranium are extracted from carnotite by direct leaching of the raw ore with sulfuric acid. An alternative method is roasting the ore followed by successive leaching with H_2O and dilute HCl or H_2SO_4. In some cases, the first leach is with a Na_2CO_3 solution. The uranium and vanadium are then separated from the pregnant liquor by liquid–liquid extraction techniques involving careful control of the oxidation states and pH during extraction and stripping.

In the Republic of South Africa, the recovery of high vanadium slags from titaniferous magnetites has been achieved on a large scale (8). The ore, containing about 1.75 wt % V_2O_5, is partially reduced with coal in large rotary kilns. The hot ore is then fed to an enclosed, submerged-arc electric smelting furnace which produces a slag containing substantial amounts of titania and pig iron containing most of the vanadium that was in the ore. After tapping from the furnace and separation of the waste slag, the molten pig iron is blown with oxygen to form a slag containing up to 25 wt % V_2O_5. The slag is separated from the metal and may then be used as a high raw material in the usual roast–leach process.

Solvent extraction following roasting and leaching is a promising processing method for dolomitic shale from Nevada (9).

4.2. Ferrovanadium. The steel industry accounts for the majority of the world's consumption of vanadium as an additive to steel. It is added in the steelmaking process as a ferrovanadium alloy [12604-58-9], which is produced commercially by the reduction of vanadium ore, slag, or technical-grade oxide with carbon, ferrosilicon, or aluminum. The product grades, which may contain 35–80 wt % vanadium, are classified according to their vanadium content. The consumer use and grade desired dictate the choice of reductant.

Carbon Reduction. The production of ferrovanadium by reduction of vanadium concentrates with carbon has been supplanted by other methods. An important development has been the use of vanadium carbide as a replacement for ferrovanadium as the vanadium additive in steelmaking. A product containing ca 85 wt % vanadium, 12 wt % carbon, and 2 wt % iron is produced by the solid-state reduction of vanadium oxide with carbon in a vacuum furnace.

Silicon Reduction. The preparation of ferrovanadium by the reduction of vanadium concentrates with ferrosilicon has been used but not extensively. It involves a two-stage process in which technical-grade vanadium pentoxide, ferrosilicon, lime, and fluorspar are heated in an electric furnace to reduce the oxide; an iron alloy containing ca 30 wt % vanadium but undesirable amounts of silicon is produced. The silicon content of the alloy is then decreased by the addition of more V_2O_5 and lime to effect the extraction of most of the silicon into the slag phase. An alternative process involves the formation of a vanadium–silicon alloy by the reaction of V_2O_5, silica, and coke in the presence of a flux in an arc furnace. The primary metal then reacts with V_2O_5 yielding ferrovanadium.

A silicon process has been developed by the Foote Mineral Company and has been used commercially to produce tonnage quantities of ferrovanadium (10). A vanadium silicide alloy containing less than 20 wt % silicon is produced in a submerged-arc electric furnace by reaction of vanadium-bearing slags with silica, flux, and a carbonaceous reducer followed by refinement with vanadium oxide. This then reacts with a molten vanadiferous slag in the presence of lime yielding a ferrovanadium alloy (Solvan) containing ca 28 wt % vanadium, 3.5 wt % silicon, 3.8 wt % manganese, 2.8 wt % chromium, 1.25 wt % nickel, 0.1 wt % carbon, and the remainder iron. A unique feature of this process is its applicability to the pyrometallurgical process of vanadium-bearing slags of the type described in the preceding section.

Aluminum Reduction. The aluminothermic process for preparing a ferrovanadium alloy differs from the carbon and silicon reduction processes in that the reaction is highly exothermic. A mixture of technical-grade vanadium oxide, aluminum, iron scrap, and a flux are charged into an electric furnace and the reaction between aluminum and vanadium pentoxide is initiated by the arc. The temperature of the reaction is controlled by adjusting the size of the particles and the feed rate of the charge by using partially reduced material or by replacing some of the aluminum with a milder reductant, eg, calcium carbide, silicon, or carbon. Ferrovanadium containing as much as 80 wt % vanadium is produced in this way.

Ferrovanadium can also be prepared by the thermite reaction, in which vanadium and iron oxides are co-reduced by aluminum granules in a magnesite-lined steel vessel or in a water-cooled copper crucible (11) (see ALUMINUM AND ALUMINUM ALLOYS). The reaction is initiated by a barium peroxide–aluminum ignition charge. This method is also used to prepare vanadium–aluminum master alloys for the titanium industry.

4.3. Pure Vanadium. Vanadium, like its sister Group 5 (VB) elements, dissolves significant quantities of oxygen, nitrogen, hydrogen, and carbon interstitially into its lattice. In so doing, a severe loss of ductility results. Formation of a ductile pure metal or alloy requires that contamination by these elements is carefully controlled. Generally, small quantities of some or all of these elements, particularly oxygen, are tolerated in a compromise between increased strength and loss of ductility. The production method for pure vanadium and vanadium-based alloys must be tailored with this need for high purity and for economic and engineering considerations in mind. Most reduction processes suffer from inabilities to reduce the amount of all impurities simultaneously to the desired level. Consequently, one or more purification methods are used to overcome the limitations of the original reduction.

Vanadium metal can be prepared either by the reduction of vanadium chloride with hydrogen or magnesium or by the reduction of vanadium oxide with calcium, aluminum, or carbon. The oldest and most commonly used method for producing vanadium metal on a commercial scale is the reduction of V_2O_5 with calcium. Recently, a two-step process involving the aluminothermic reduction of vanadium oxide combined with electron-beam melting has been developed. This method makes possible the production of a purer grade of vanadium metal, ie, of the quality required for nuclear reactors (qv).

Calcium Reduction. High purity vanadium pentoxide is reduced with calcium to produce vanadium metal of ca 99.5% purity. The exothermic reaction is carried out adiabatically in a sealed vessel or bomb. In the original process, calcium chloride was added as a flux for the CaO slag (12). The vanadium metal was recovered in the form of droplets or beads. A massive ingot or regulus has been obtained by replacing the calcium chloride flux with iodine (13). This latter reaction became the basis of the first large-scale commercial process for producing vanadium. The reaction is initiated either by preheating the charged bomb or by internal heating with a fuse wire embedded in the charge. Calcium iodide formed by the reaction of calcium with iodine serves both as a flux and as a thermal booster. Thus, sufficient heat is generated by the combined reactions to yield liquid metal and slag products. The resulting metal contains ca 0.2 wt % carbon, 0.02–0.8 wt % oxygen, 0.01–0.05 wt % nitrogen, and 0.002–0.01 wt % hydrogen. Two factors that contribute to the relative inefficiency of this process are the rather low metal yields (75–80%) and the required amount of calcium reductant (50–60% excess of stoichiometric quantity).

Vanadium powder can be prepared by substituting V_2O_3 for the V_2O_5 as the vanadium source. The heat generated during the reduction of the trioxide is considerably less than for the pentoxide, so that only solid products are obtained. The powder is recovered from the product by leaching the slag with dilute acid.

Aluminothermic Process. In the development of the liquid-metal fast-breeder reactor, vanadium has been considered for use as a fuel-element cladding material (see NUCLEAR REACTORS). Difficulty was encountered in the fabrication of alloys prepared from the calcium-reduced metal, a factor attributable to the high interstitial impurity content. An aluminothermic process was developed by the AEC (now the NRC) in order to meet the more stringent purity requirements for this application (14). In this process, vanadium pentoxide reacts with high purity aluminum in a bomb to form a massive vanadium–aluminum alloy. Use of proprietary additions to either increase the reaction temperature, decrease the melting point of the slag or metal, or increase the fluidity of the two phases leads to formation of a solid metallic regulus that is relatively free of slag. The alloyed aluminum and dissolved oxygen are subsequently removed in a high temperature, high vacuum processing step to yield metal of greater than 99.9% purity.

Purified V_2O_5 powder and high purity aluminum granules are charged into an alumina-lined steel crucible. The vessel is flushed with an inert gas to minimize atmospheric contamination and then is sealed. The reaction is initiated by a vanadium fuse wire. Sufficient heat is generated by the chemical reaction to produce a molten alloy of vanadium containing ca 15 wt % aluminum; a fused aluminum oxide slag also forms. The liquid alloy separates from the alumina slag and settles to the bottom of the crucible as a massive product. The feasibility of carrying this reaction out in a water-cooled copper crucible, thus eliminating the alumina liner which is a source of some contamination, has been demonstrated.

Examination of the metallic product (regulus) of such aluminothermically produced vanadium metal reveals the presence of oxide phases in the metal matrix. This suggests that there is a decreasing solubility for aluminum and oxygen below the melting point. To date, no purification processes have been developed that take advantage of the purification potential of this phenomenon.

The vanadium alloy is purified and consolidated by one of two procedures, as shown in the flow diagram of the entire aluminothermic reduction process presented in Figure 1. In one procedure, the brittle alloy is crushed and heated in a vacuum at 1790°C to sublime most of the aluminum, oxygen, and other impurities. The aluminum facilitates removal of the oxygen, which is the feature that makes this process superior to the calcium process. Further purification and consolidation of the metal is accomplished by electron-beam melting of pressed compacts of the vanadium sponge.

The alternative procedure involves direct electron-beam melting of the vanadium–aluminum alloy regulus. Two or more melting steps are required to achieve the desired levels of aluminum and oxygen in the final ingot. Chemical analyses of two ingots of vanadium metal prepared from the identical vanadium–aluminum alloy and processed by the two methods described above are presented in Table 4. Comparable purities are obtained by these procedures. Ingots weighing up to 454 kg have been prepared by this process involving direct electron-beam melting of the alloy.

4.4. Refining of Vanadium. In addition to the purification methods described above, vanadium can be purified by any of three methods: iodide refining (van Arkel-deBoer process), electrolytic refining in a fused salt, and electrotransport.

Metal of greater than 99.95% purity has been prepared by the iodide-refining method (15). In this process, an impure grade of vanadium metal reacts with iodine at 800–900°C forming vanadium diiodide and the volatilized iodide is thermally decomposed and deposited on a hot filament at ca 1300°C. The refining step is carried out in an evacuated and sealed tube. The main impurities removed in the process are the gaseous elements and those metals that form stable or nonvolatile iodides. Vanadium metal containing 5 ppm nitrogen, 150 ppm carbon, and 50 ppm oxygen has been prepared in this way.

An electrolytic process for purifying crude vanadium was developed at the U.S. Bureau of Mines (16). It involves the cathodic deposition of vanadium from an electrolyte consisting of a solution of VCl_2 in a fused KCl–LiCl eutectic. The vanadium content of the mixture is 2–5 wt % and the operating temperature of the cell is 650–675°C. Metal crystals or flakes of up to 99.995% purity have been obtained by this method.

The highest purity vanadium reported has been purified by an electrotransport technique (17). A high density current is passed through a small rod of electrolytically refined metal, heating it to 1700–1850°C. Under these conditions, interstitial solute atoms, eg, carbon, oxygen, and nitrogen, migrate to the negative end of the bar, which results in a high degree of purification along the remainder of the rod. Small amounts of vanadium containing less than 10 ppm of carbon, oxygen, and nitrogen and having a resistance ratio, $R_{300\ K}:R_{4.2\ K}$, of greater than 1100 have been prepared by this technique.

5. Consolidation and Fabrication

Because no process has been developed for selectively removing impurities in vanadium and vanadium alloys in the metallic state, it is essential that all starting materials, in aggregate, be pure enough to meet final product purity requirements. In addition, the consolidation method must be one that prevents contamination through reaction with air or with the mold or container material.

5.1. Consolidation.

Consolidation by the consumable-electrode electric-arc melting technique is ideally suited for vanadium and is used extensively for preparation of ingots of most of the reactive and refractory metals (18,19). An electrode consisting of carefully weighed portions of each alloy constituent is prepared by combining various sizes and shapes of starting materials. For example, an alloy composed of vanadium plus 15 wt % titanium and 7.5 wt % chromium might consist of an electron-beam purified vanadium ingot to which has been welded high purity titanium plat and electrolytically produced chromium granules. Welding is performed either in a vacuum or under an inert gas, eg, argon, helium, or a mix of the two.

The electrode is attached mechanically and electrically to a system that feeds it downward as well as in all horizontal directions so as to center the electrode in the crucible. The electrode is then placed in a water-cooled copper crucible whose internal diameter is 2.5–7.6 cm greater than the circle circumscribing the electrode. Chips or blocks of vanadium or of the alloy to be melted are placed in the bottom of the crucible, forming a starter pad for the arc melting. The furnace assembly is sealed and the chamber evacuated and then backfilled with a pressure of helium and argon, which varies from between a few millipascals (10^{-5} mm Hg) to nearly 101.3 kPa (=1 atm). An arc is struck between the electrode and the starter pad; voltage and amperage are varied to control the energy input and, thus, the rate at which the electrode is melted and consumed to form the alloy ingot.

Multiple-arc melting for a minimum of two melts is conventionally used to ensure a homogeneous ingot. Although conventional arc-melt practice involves a negative electrode, improved alloying is achieved with a positive electrode for at least one of the several melts and usually the first melt.

The as-cast ingot generally exhibits a rough side wall because of entrapment of porosity as the molten metal contacts the water-cooled copper crucible. Also, a shrinkage cavity usually forms near the top of the ingot as a result of volumetric changes during solidification. Both of these artifacts are normally removed prior to fabrication, because most vanadium alloys exhibit only limited ductility in the as-cast condition, and the porosity, if not removed, would lead to cracking. Machining is the conventional surface-conditioning method.

5.2. Fabrication.

Primary or initial fabrication is generally performed by either forging or extrusion at 1000–1200°C (19). Because the alloy oxidizes quite rapidly at elevated temperatures and because the pentoxide melts at 690°C, the machined ingot is clad and sealed in a mild-steel container. Following the initial hot-working sequences, subsequent working can be performed at RT to 500°C, depending on the alloy and the stage of processing. Intermediate and final recrystallization annealing are performed at 650–1000°C. Annealing is done in a vacuum or inert gas to reduce metal loss and contamination of the metal which would occur if heating were done in air.

The fabrication of most vanadium alloys is difficult because of increased strength and decreased ductility, especially at low temperatures. Generally, higher temperatures are used for each step of fabrication. Also, processes, eg, extrusion in which the forces are largely compressive, are used for the initial ingot breakdown.

6. Economic Aspects

Nearly all the world's supply of vanadium is from primary sources. Table 5 lists world mine production, reserves, and reserve bases for vanadium (20). Table 6 gives United States statistics for vanadium (20).

Metallurgical applications continue to dominate in the United States, accounting for 95% of reported consumption. Nonmetallurgical applications include catalysts, ceramics, electronics, and vanadium chemicals (21).

Strong demand for vanadium led to a surge in pricing even though production also increased in 2004. Surging steel production and a move towards higher strength steels in China were the coupled with a strong demand for high strength and specialty steel in the United States were the driving forces. Demand outstripped supply in both 2003 and 2004, but the deficit was made up from stocks which had risen to 23,000 t in 2002 (22). The world vanadium reserve base, at more than 38×10^6 t, is sufficient to meet vanadium demand into the next century at present demand. This does not account for the increased recovery of vanadium from fly ash, petroleum residues, slag and spent catalysts that will extend the life of the reserve base significantly.

7. Health and Safety Factors, Toxicology

In the consolidated form, vanadium metal and its alloys pose no particular health or safety hazard. However, they do react violently with certain materials, including BrF_3, chlorine, lithium, and some strong acids (23). As is true with many metals, there is a moderate fire hazard in the form of dust or fine powder or when the metal is exposed to heat or flame. Since vanadium reacts with oxygen and nitrogen in air, control of such fires normally involves smothering the burning material with a salt.

Vanadium compounds, including those which may be involved in the production, processing, and use of vanadium and vanadium alloys, are irritants chiefly to the conjuctivae and respiratory tract. Prolonged exposure may lead to pulmonary complications. However, responses are acute, never chronic. Toxic effects vary with the vanadium compound involved. For example, LD_{50} (oral) of vanadium pentoxide dust in rats is 23 mg/kg of body weight (23).

The toxicity of vanadium alloys may depend on other components in the alloy. For example, the V_3Ga alloy requires precautions related to both vanadium and gallium, and gallium is highly toxic. Similarly, alloys with chromium may require precautions associated with that metal.

These limits are for normal 8-h workday and 40-h work-week exposures. The short-term exposure limit (STEL) is 1.5 mg/m^3 for dusts (24). OSHA PEL for respirable dust and fume is TWA 0.05 mg (V_2O_5)/m^3; NIOSH REL TWA = 1.0 mg (V)/m^3 (23). A description of health hazards, including symptoms, first aid, and organ involvement, personal protection, and respirator use has been published (25).

The ammonium salts of vanadic acid and vanadium pentoxide have been listed as toxic constituents in solid wastes under the Resource Conservation and Recovery Act (26).

8. Uses

The most important use of vanadium is as an alloying element in the steel industry where it is added to produce grain refinement and hardenability in steels. Vanadium is a strong carbide former, which causes carbide particles to form in the steel, thus restricting the movement of grain boundaries during heat treatment. This produces a fine-grained steel which exhibits greater toughness and impact resistance than a coarse-grained steel and which is more resistant to cracking during quenching. In addition, the carbide dispersion confers wear resistance, weldability, and good high temperature strength. Vanadium steels are used in dies or taps because of their deep-hardening characteristics and for cutting tools because of their wear resistance. They are also used as constructional steel in light and heavy sections; for heavy iron and steel castings; forged parts, eg, shafts and turbine motors; automobile parts, eg, gears and axles; and springs and ball bearings. Vanadium is an important component of ferrous alloys used in jet-aircraft engines and turbine blades where high temperature creep resistance is a basic requirement (see HIGH TEMPERATURE ALLOYS).

The principal application of vanadium in nonferrous alloys is the titanium 6–4 alloy (6 wt % Al–4 wt % V), which is important in supersonic aircraft where strength-to-weight ratio is a primary consideration. Vanadium and aluminum impart high temperature strength to titanium, a property that is essential in jet engines, high speed air frames, and rocket-motor cases. Vanadium foil can be used as a bonding material in the cladding of titanium to steel. Vanadium is added to copper-based alloys to control gas content and microstructure. Small amounts of vanadium are added to aluminum alloys to be used in pistons of internal combustion engines to enhance the alloy's strength and reduce their thermal expansion coefficients. Because of its low capture cross section for fast neutrons as well as its resistance to corrosion by liquid sodium and its good high temperature creep strength, vanadium alloys are receiving considerable attention as a fuel-element cladding for fast-breeder reactors. Vanadium is a component in several permanent-magnet alloys containing cobalt, iron, sometimes nickel, and vanadium. The vanadium content in the most common of these alloys is 2–13 wt % (see Magnetic Materials). Nonmetallurgical applications include catalysts, ceramics, electronics, and vanadium chemicals.

8.1. Superconductivity. One potential use of vanadium is in the field of superconductivity. The compound V_3Ga exhibits a critical current at 20 T (20×10^4 G), which is one of the highest of any known material. Although niobium–zirconium and Nb_3Sn have received more attention, especially in the United States, the vanadium compound is being studied for possible future application in this field since V_3Ga exhibits a critical temperature of 15.4 K as opposed to 18.3 K for Nb_3Sn.

Like Nb_3Sn, V_3Ga has a Type A15 structure, which exhibits low ductility. Consequently, efforts at producing the compound in fine-grained fibrous structures have involved unique processing techniques (27). One method consists of forming a billet consisting of vanadium rods surrounded by a Cu–Ga bronze alloy. The billet is fabricated to wire by conventional extrusion, rod-rolling, or swagging and wire-drawing techniques. Following production of a wire, a heat treatment is performed which leads to diffusion of Ga to the fine V filaments, thereby forming the V_3Ga intermetallic compound.

Another technique, developed originally for Cu–Nb alloys, begins by rapidly chilling a liquid Cu–V alloy. During solidification, a fine dispersion of primary vanadium grains form in the matrix of the Cu–V alloy. The cast billet is fabricated by the methods described above. Following formation of the wire, gallium is plated on it and thermally diffuses, forming the V_3Ga which is in long, thin platelets ca 0.01–0.1 μm dia.

8.2. Fusion Reactors. The development of fusion reactors requires a material exhibiting high temperature mechanical strength, resistance to radiation-induced swelling and embrittlement, and compatibility with hydrogen, lithium and various coolants. One alloy system that shows promise in this application, as well as for steam-turbine blades and other applications in nonoxidizing atmospheres, is based on the composition $(Fe,Co,Ni)_3V$ (28). Through control of an ordered–disordered transformation, the yield strength of these alloys increases at elevated temperatures above the room-temperature yield strength. One composition, for example, exhibits a yield strength of 480 MPa (70,000 psi) at ca 750°C compared to its room temperature value of 345 MPa (50,000 psi). The alloys also show good resistance to radiation-induced swelling (see FUSION ENERGY). These alloys can be fabricated, eg, by rolling, at 1000–1100°C and are then heat-treated at 800–1100°C.

Table 7 lists the U.S. consumption of vanadium by end use and form for 2003–2004.

8.3. New Research. McKenzie Bay International is building an “integrated products for energy” organization based on a new vanadium-base electricity storage device and alternative electrical power generation systems. McKenzie Bay continued development of the WindStor renewable energy generation, storage, and distribution system. The WindStor system uses a vertical wind turbine (WWT) with vanadium-base batteries and a proprietary system integrator to provide stored electricity to users. If the 100-kw prototypes tested in 2005 performed well, the company intends to manufacture WWTs for commercial introduction (29). Medical uses for vanadium are mentioned in the patent literature. For example drugs using vanadium compounds to fight diabetes (30) and cancer (31) have been reported.

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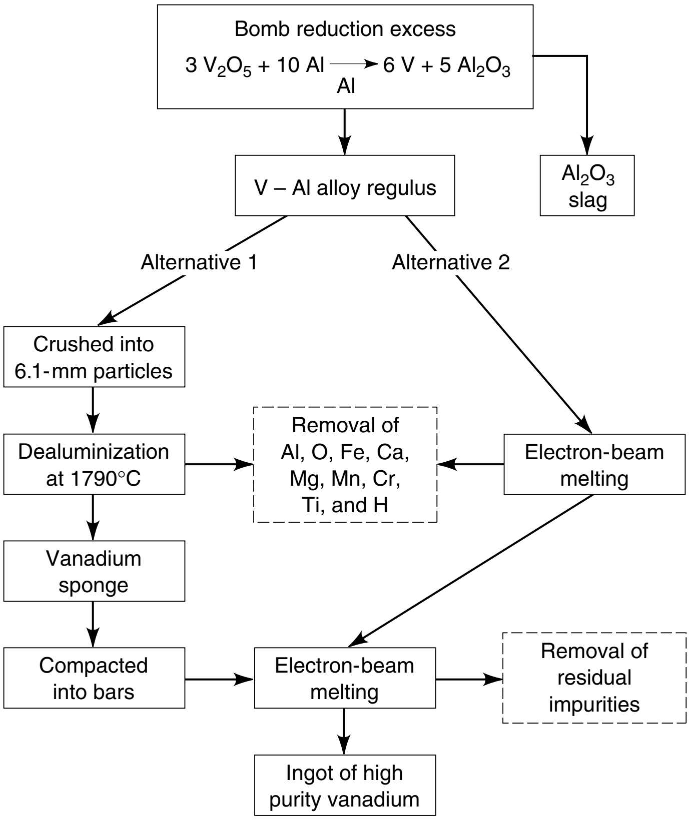

Fig. 1. Flow diagram for aluminothermic process showing alternative methods of aluminum removal from alloy regulus.

Table 1. **Important Minerals of Vanadium**

Mineral	CAS Registry Number	Color	Formula	Location
patronite	[12188-60-2]	greenish black	$V_2S + nS$	Peru
bravoite	[12172-92-8]	brass	$(Fe,Ni,V)S_2$	Peru
sulvanite	[15117-74-5]	bronze-yellow	$3Cu_2S \cdot V_2S_6$	Australia, United States (Utah)
davidite	[12173-20-5]	black	titanate of Fe, U, V, Cr, and rare earths	Australia
roscoelite	[12271-44-2]	brown	$2K_2O \cdot 2Al_2O_3 (Mg,Fe)O \cdot \text{-} 3V_2O_5 \cdot 10SiO_2 \cdot 4H_2O$	United States (Colorado, Utah)
carnotite	[1318-26-9]	yellow	$K_2O \cdot 2U_2O_3$, $V_2O_5 \cdot 3H_2O$	southwest United States
vanadinite	[1307-08-0]	reddish brown	$Pb_5(VO_4)_3Cl$	Mexico, United States, Argentina
descloizite	[19004-61-6]	cherry-red	$4(Cu,Pb,Zn)O \cdot V_2O_5 \cdot H_2O$	Namibia, Mexico, United States
cuprodescloizite	[12325-36-9]	greenish brown	$5(Cu,Pb)O \cdot (V,As)_2O_5 \cdot 2H_2O$	Namibia
vanadiferous phosphate rock			$Ca_5(PO_4)_3(F,Cl,OH)$; VO_4 ions replace some PO_4 ions	United States (Montana)
titaniferous magnetite			$FeO \cdot TiO_2 - FeO \cdot (Fe,V)O_2$	Russia, People's Republic of China, Finland, Union of South Africa

Table 2. **Physical Properties of Vanadium Metal**[a]

Property	Value
melting point, °C	1890 ± 10
boiling point, °C	3380
vapor pressure, from 1393–1609°C, kPa[b]	$R\ln P = \frac{121,950}{T} - 5.123 \times 10^{-4}\,T + 38.3$
crystal structure	bcc
lattice constant, nm	0.3026
density, g/cm^3	6.11
specific heat, 20–100°C, J/g[c]	0.50
latent heat of fusion, kJ/mol[c]	16.02
latent heat of vaporization, kJ/mol[c]	458.6
enthalpy, at 25°C, kJ/mol[c]	5.27
entropy, at 25°C, kJ/(mol·°C)[c]	29.5
thermal conductivity, at 100°C, W/(cm·K)	0.31
electrical resistance, at 20°C, μΩ·cm	24.8–26.0
temperature coefficient of resistance, at 0–100°C, (μΩ·cm)/°C	0.0034
magnetic susceptibility, m^3/mol[d]	0.11
superconductivity transition, K	5.13
coefficient of linear thermal expansion, $°C^{-1}$	
at 20–720°C (x-ray)	$(9.7 \pm 0.3) \times 10^{-6}$
200–1000°C (dilatometer)	8.95×10^{-6}
thermal expansion, at 23–100°C, $\times 10^{-6}/°C$	8.3
recrystallization temperature, °C	800–1000
modulus of elasticity, MPa[e]	$(1.2–1.3) \times 10^5$
shear modulus, MPa[e]	4.64×10^4
Poisson ratio	0.36
thermal neutron absorption, m^2/at.[f]	$(4.7 \pm 0.02) \times 10^{-28}$
capture cross section for fast (1 MeV) neutrons, m^2/at.[f]	3×10^{-31}

[a] Refs. 4–6.

[b] To convert kPa to atm, divide by 101.3. In this, the Antoine equation, R = gas constant, T is temperature in K, and P is pressure in kPa.

[c] To convert J to cal, divide by 4.184.

[d] To convert m^3/mol to cgs units, multiply by $4\pi \times 10^{-6}$.

[e] To convert MPa to psi, multiply by 145.

[f] To convert m^2 to barns, multiply by 1×10^{28}.

Table 3. **Typical Room Temperature Properties of Vanadium and Vanadium Alloys**[a]

Metal	Tensile strength, MPa[b]	Yield strength, MPa[b]	Elongation, %
pure vanadium			
annealed or hot-worked	380–550	410–480	20–27
cold-worked	910	760	2–7
alloys			
V 87.5, Ti 15, Cr 7.5 annealed	730	620	30
V 80, Cr 15, Ti 5 annealed	600	500	28
various high strength alloys, warm rolled	1210		2–5

[a] Refs. 3 and 6.

[b] To convert MPa to psi, multiply by 145.

Table 4. **Vanadium Prepared by Dealuminization with Vacuum Heating**[a]

	By dealuminization, ppm		By direct melting, ppm	
Impurity	Sponge	Electron-beam melted ingot	First melt	Second melt
C	100	100	100	100
O	50	60	200	150
N	40	45	40	50
H	<1	<1	<1	<1
Al	>1000	300	ca 1000	100
Ca	<10	<10	<10	<10
Cu	<20	<20	<20	<20
Fe	70	70	60	60
Mg	<20	<20	<20	<20
Mn	<20	<20	<20	<20
Ni	60	60	60	60
Si	300	300	300	300

[a] Compared to that prepared by direct electron-beam melting of vanadium alloy containing 15 wt % aluminum.

Table 5. **World Mine Production, Reserves, and Reserve Base for Vanadium, $\times 10^3$ t**[a]

	Mine production		Reserves	Reserve base
Country	2004	2005[b]		
United States			45	4,000
China	14	14.5	5,000	14,000
Russia	8	9	5,000	7,000
South Africa	17.2	18	3,000	12,000
other countries	1	1	NA[c]	1,000
World total (rounded)	*40.2*	*42.5*	*13,000*	*38,000*

[a] Ref. 20.

[b] Estimated.

[c] NA = not available.

Table 6. **U.S. Statistics for Vanadium,** ×10^3 t[a]

Salient Statistics	2001	2002	2003	2004	2005[b]
production, mine, mill					
imports for consumption:					
ash, ore, residues, slag	1,670	1,870	3,060	2,350	3,370
vanadium pentoxide, anhydride	804	455	679	1,230	1,520
oxides and hydroxides, other	57	66	74	133	234
aluminum-vanadium master alloys (gross weight)	10	98	232	19	
ferrovanadium	2,550	2,520	1,360	3,020	4,460
exports:					
vanadium pentoxide, anhydride	71	91	185	240	232
oxides and hydroxides, other	63	203	284	584	819
aluminum-vanadium master alloys (gross weight)	363	529	677	887	1920
ferrovanadium	70	142	397	267	488
consumption, reported	3,210	3,080	3,240	4,050	4,180
price, average, dollars per pound V_2O_5	1.37	1.34	2.21	5.28	17.50
stocks, consumer, yearend	251	221	250	305	275
employment, mine and mill, number					
net import reliance as a percentage of reported consumption	100	100	100	100	100

[a] Ref. 20.

[b] Estimated.

Table 7. **U.S. Consumption of Vanadium by End Use and Form kg of Contained Vanadium**[a,b]

	2003	2004
End use		
steel:		
carbon	1,030,000	1,300,000
full alloy	808,000	1,060,000
high-strength low-alloy	938,000	1,160,000
stainless and heat resisting	69,500	60,000
tool	143,000	239,000
Total	*2,990,000*	*3,820,000*
cast irons	W	W
superalloys	13,100	16,600
alloys (excluding steels and superalloys):		
welding and alloy hard-facing rods and materials	W	W
other alloys[c]	W	W
chemical and ceramic uses:		
catalysts	W	W
pigments	W	W
miscellaneous and unspecified	240,000	215,000
Grand total	*3,240,000*	*4,050,000*
Form		
ferrovanadium	2,910,000	3,610,000
oxide	238,000	269,000
other[d]	93,100	180,000
Total	*3,240,000*	*4,050,000*

[a] Ref. 21.

[b] W = withheld to avoid disclosing company proprietary data; included with "Miscellaneous and unspecified."

[c] Includes magnetic alloys.

[d] Consists principally of vanadium-aluminum alloy, small quantities of other vanadium alloys, vanadium metal, and ammonium metavanadate.