

Technology of Vanadium Ferroalloys

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Chapter Outline

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13.1 PROPERTIES OF VANADIUM AND ITS COMPOUNDS

Vanadium is an element of the fifth group of the periodic table. Its serial number is 23, its atomic weight is 50.94, and its external electron configuration is $3d^3 4s^2$, which allows it to take valence states from +2 to +5. The melting temperature of pure vanadium is 1920°C, the boiling point is ~3400°C, and its density at 20°C is 6.11 g/cm³. Because of its high melting point, vanadium belongs to the refractory metals group (niobium, tantalum, chromium,

molybdenum, tungsten). Like most of the refractory elements, pure vanadium is ductile, but impurities usually make it brittle.

Vanadium is mainly used as an alloying addition to steel (already at 0.01% to 0.05% V), as it promotes the formation of finer grain size, increases hardenability, and improves wear resistance through the precipitation of its carbides and nitrides (vanadium is a strong carbide former, which causes carbide particles to form in the steel). These features are used in a large variety of steels (constructional grades, carburizing steels, rail steels, and especially in heat-resisting tool and die steels and special stainless steels). Vanadium is also an important beta-phase stabilizer for titanium alloys and other special alloys widely used in turbine motors, automobile parts, jet-aircraft engines, and so on, where high temperature creep resistance is a basic requirement (Baroch, 2005).

With iron, vanadium forms a continuous series of BCC (ferrite type) solid solutions with a minimum melting temperature (Fig. 13.1). Below 1250°C there is an area of σ -phase in a wide temperature range, which is similar to one forming in the Fe-Cr system.

In the system V-C (Fig. 13.2), there are three known vanadium carbides, of which V_2C and VC are rather refractory and have a substantial homogeneity range (somewhat similar to the W-C system).

With silicon, vanadium forms several silicides (Fig. 13.3), known as V_3Si , V_5Si_3 , V_6Si_5 , and VSi_2 , of which V_3Si has a noticeable homogeneity region around 21.4% to 25% (at.) Si.

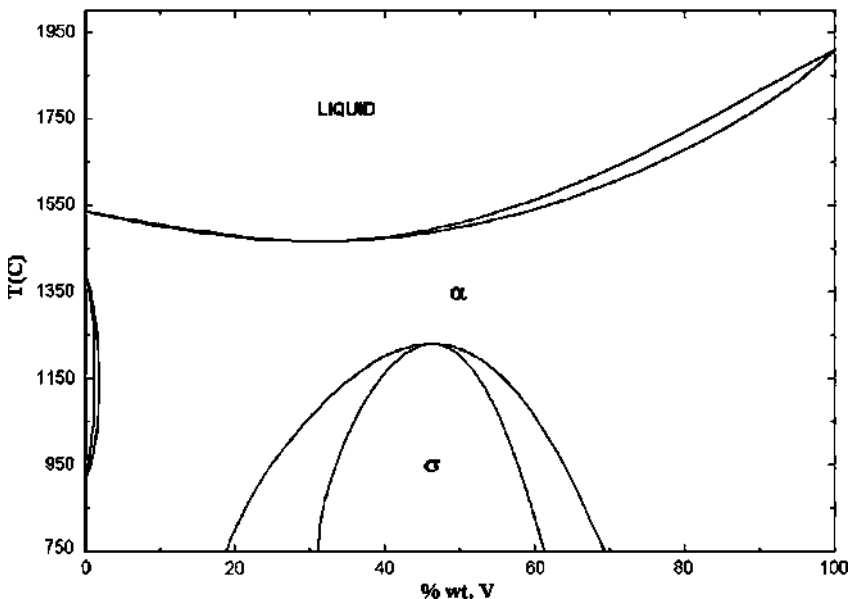


FIGURE 13.1 Equilibrium phase diagram of the Fe-V system.

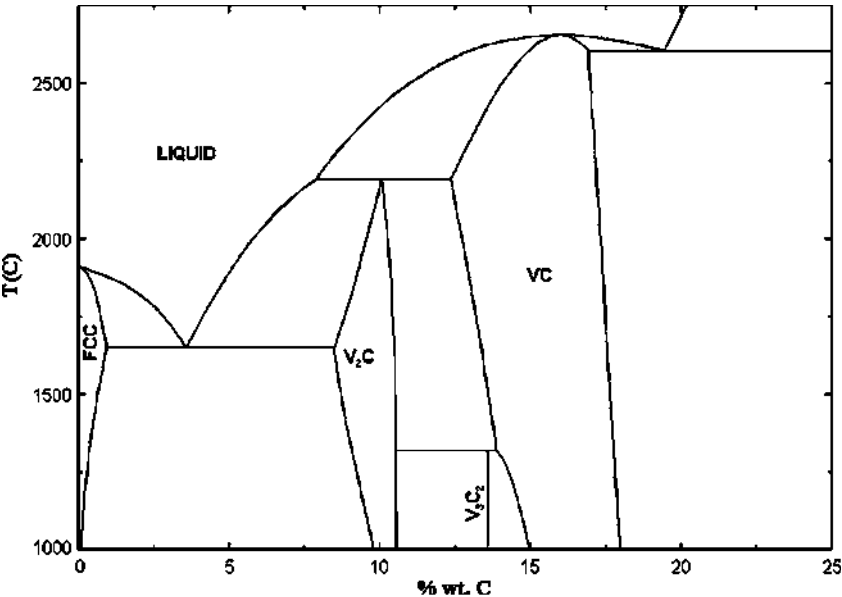


FIGURE 13.2 Diagram of the equilibria in the V-C system.

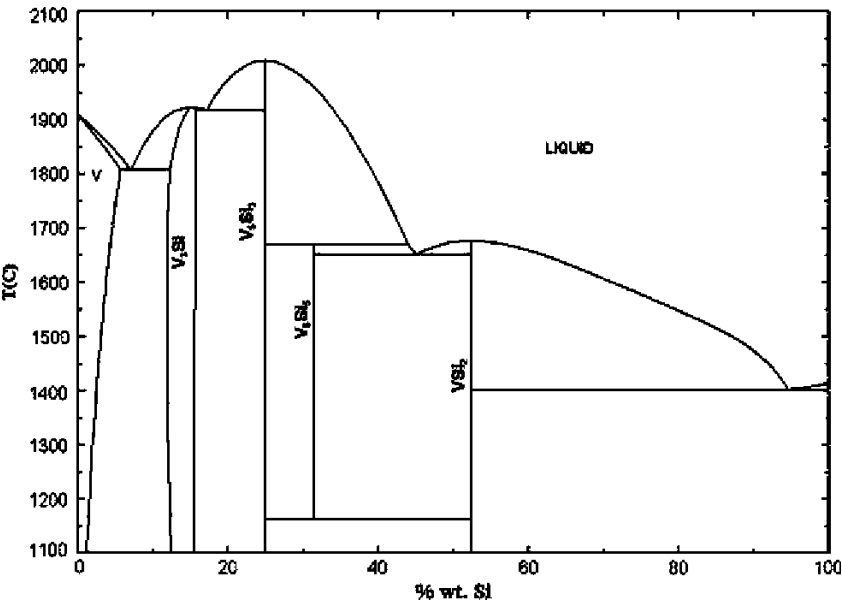


FIGURE 13.3 Diagram of the equilibria in the V-Si system.

Several intermetallics are known in the system V-Al (Fig. 13.4). Aluminide V_5Al_8 is the most refractory of those intermetallics.

The system V-O (Fig. 13.5) is rather complex, resembling similar equilibria in the Ti-O system. The most stable vanadium oxides are δ -VO, V_2O_3 and V_2O_5 . The density of oxide VO is 5.76 g/cm^3 , the density of V_2O_3 is 4.87 g/cm^3 , and the density of V_2O_5 is 3.36 g/cm^3 . With the increase in the oxidation state of vanadium, its oxides acquire more enhanced acidic properties and their overall chemical resistance increases. The higher vanadium oxides (Magnelli phases, as in the case of the Ti-O or Mo-O system) might be expressed by the common formulas V_nO_{2n-1} ($n=3-6$) and V_nO_{2n+1} ($n=3$ and 6). As Figure 13.5 shows, many vanadium oxides are characterized by rather wide homogeneity ranges.

Vanadium oxides form with iron oxide spinel FeV_2O_4 and $2FeO \cdot V_2O_3$ as well as a series of solid solutions with a wide range of homogeneities. With CaO, vanadium pentoxide has three known vanadates ($CaO \cdot V_2O_5$, $2CaO \cdot V_2O_5$, and $3CaO \cdot V_2O_5$) and at least five nonvariant equilibria and three eutectics, but this system has not yet been well studied throughout its concentration range. With alumina, V_2O_5 has one compound, $Al_2O_3 \cdot V_2O_5$ ($AlVO_4$), which melts incongruently at 695°C . Vanadium compounds are present in ores and slags in different forms, and it is customary to recalculate the amount of vanadium on the V_2O_5 basis.

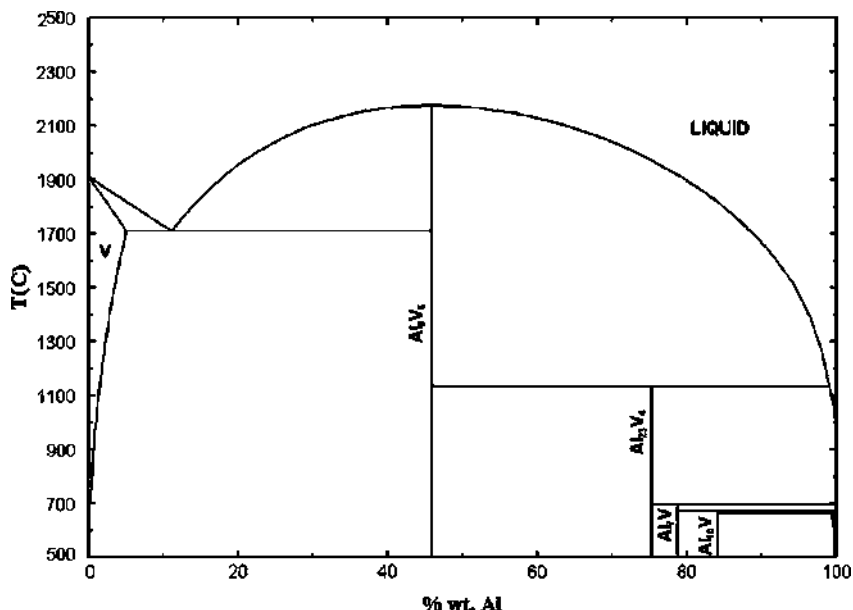


FIGURE 13.4 Equilibrium phase diagram in the V-Al system.

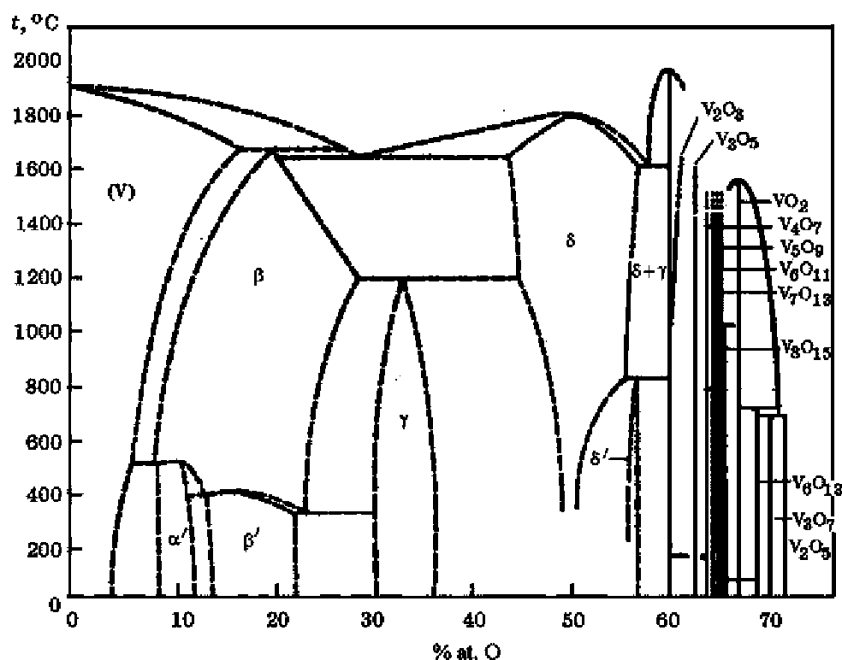


FIGURE 13.5 Combined diagram of the equilibria in the V-O system: α' - V_2O_5 , β , β' - V_2O_4 , γ - V_2O_4 , and δ -VO.

13.2 SOURCES OF VANADIUM

Although it is abundant in Earth's crust and oil deposits, vanadium is, however, present in concentrations that make it too uneconomical to process it alone. Thus, most vanadium coming from primary sources is usually co-produced along with the recovery of other minerals or substances. Estimated world vanadium reserves are considered to be sufficient to meet vanadium demand into the 21st century based on the present demand. This does not account for the increased recovery of vanadium from fly ash, petroleum residues, slag, and spent catalysts (Baroch, 2005).

The most important minerals of vanadium are shown in Table 13.1. The vanadium minerals of industrial importance are mainly titanomagnetite, kulsonite, roscoelite, and carnotite. Industrial sources of vanadium are usually classified into the following groups and subgroups:

1. Vanadium ores, where vanadium might be considered to be the leading element ($>3\%$ V_2O_5), usually a subgroup of roscoelite
2. Complex vanadium ores of nonferrous and rare metals, 1% to 3% V_2O_5 (carnotite, vanadium bauxite)

TABLE 13.1 Some Important Minerals of Vanadium

Mineral/Group	Approximate Formula
Sulfides	
Patronite	V_2S
Bravoite	$(Fe, Ni, V)S_2$
Sulvanite	$3Cu_2S \cdot V_2S_6$
Oxides	
Davidite	$(Fe, Cr)(Ti, U, V, RE)O_3$
Roscoelite	$K(V, Al, Mg)_3(AlSi_3)O_{10}(OH)_2$
Kulsonite	$(Fe, V)_3O_4$
Carnotite	$K_2(UO_2)_2(VO_4) \cdot 3H_2O$
Vanadinite	$Pb_5(VO_4)_3Cl$
Descloizite	$4(Cu, Pb, Zn)O \cdot V_2O_5 \cdot H_2O$
Cuprodescloizite	$5(Cu, Pb)O \cdot (V, As)_2O_5 \cdot 2H_2O$
Vanadiferous phosphate rock	$Ca_5(PO_4, VO_4)_3(F, Cl, OH)$
Titaniferous magnetite	$(Fe, V, Ti)_3O_4$

3. Ferrous ores with $<1\%$ V_2O_5 (magnetite, titanomagnetite, oolitic limonite),
4. Other fossil fuels $<1\%$ V_2O_5 (mostly of petrochemical origin such as asphaltites, bitumen, shale oil, coal, some phosphates).

Most world vanadium ore deposits are located in South Africa, the United States, Russia, Australia, China, Mexico, and Venezuela, but vanadium can be recovered at any large-scale petrochemical industry (Xiao et al., 2010). A recently mapped Siberian deposit (in the Baikal–Amur region of Russia) was found to hold a substantial reserve of vanadium (more than 50 million tons), making this field somewhat unique in the world. This ore contains 25% to 35% Fe, 4% to 7% TiO_2 , and 0.35% to 0.55% V_2O_5 (Gasik et al., 2009). Other potentially relevant impurities in this ore are copper (0.01% to 0.40%), cobalt, platinum, and palladium.

13.3 TREATMENT OF VANADIUM RAW MATERIALS

The main source of vanadium for metallurgy is titanomagnetite ores, which are dressed into enriched concentrates (see the example in Table 13.2) for

TABLE 13.2 Chemical Composition, %, Vanadium Ores and Concentrates

	Fe ₂ O ₃	V ₂ O ₅	TiO ₂	SiO ₂	Cr ₂ O ₃	Al ₂ O ₃	MnO	CaO	MgO	P	S
Ore (Russia)	32–38	0.1–0.7	4–14	4–16	<0.7	4–12	<0.3	2–7	4–8	0.01–0.02	0.01–0.06
Ore (Ukraine)	53–55	0.1–0.15	—	20	—	8	5	2	0.4	1	0.2
Concentrates	53–69	0.5–8	2–15	6–11	<0.1	2–7	<0.4	1–3	0.9–3	0.01–0.4	<0.04

metallurgical processing to produce V_2O_5 and ferrovandium (Gasik et al., 2009) as well as vanadium-bearing slags (Lindvall et al., 2010).

The industrial technology of vanadium extraction from the titanomagnetite is based on multistep metallurgical and chemical repartitions obtaining commercial vanadium pentoxide (V_2O_5). In addition, vanadium is often recovered from uranium–vanadium ores and from ferrophosphorus as a by-product in the production of elemental phosphorus (Baroch, 2005), as well as from petroleum products (Xiao et al., 2010).

13.3.1 Chemical Treatment of Vanadium Raw Materials

Vanadium ores are usually crushed, ground, screened, mixed with NaCl or Na_2CO_3 (soda), and roasted at 850° to $1100^\circ C$ for 2 to 3 hours. The purpose of roasting is to oxidize iron and vanadium components to the highest oxidation degree and to convert vanadium into the water-soluble form ($NaVO_3$). Sodium vanadate is readily soluble in water and in dilute acids and carbonates. Leaching of vanadium compounds from the calcined mixture is carried out in two stages with the precipitation of V_2O_5 . The first extract is treated with sulfuric acid to precipitate sodium hexavanadate ($Na_4V_6O_7$) at $pH = 2-3$, which together with other impurities forms a “red cake.” This product is converted to vanadium pentoxide of technical grade (87% to 90% V_2O_5 , 0.010% to 0.015% P, with the balance consisting mostly of Na_2O) by heating to 700° to $1000^\circ C$. To obtain higher purity, the second stage is used, whereby this red cake is treated with soda solution and purified from Fe, Al, Si, and other impurities first by pH adjustment. Finally, ammonium vanadate is precipitated and calcined to yield $>99.5\%$ V_2O_5 product (Baroch, 2005). In principle, a similar method is used for vanadium extraction from carnotite (together with uranium), but additionally there is usually a liquid–liquid extraction stage for vanadium and uranium separation.

13.3.2 Metallurgical Processing of Vanadium Raw Materials

Two main routes are used industrially for vanadium processing by metallurgical means: pig iron smelting in blast furnaces and pig iron smelting in submerged arc furnaces, followed by oxygen conversion into vanadium-rich slag. For the blast furnace technology (Gasik et al., 2009), there are some peculiarities compared to the conventional smelting of pig iron. For a more complete transition of vanadium in iron, the process is carried out at 1300° to $1350^\circ C$, and the basicity of slag is maintained at 0.8 to 0.9. The resulting cast iron contains $\sim 0.45\%$ V, 0.1% to 0.4% Si, and 0.2% to 0.3% Ti. About 80% to 85% of vanadium is reduced into the cast iron. This metal is blown by oxygen into converters producing slag with 12% to 24% V_2O_5 , 20% to 25% SiO_2 , and 30% to 45% FeO. The major form of vanadium in these slags is V^{3+} in vanadium spinels $(Fe,Mn,Mg)O \cdot (V,Fe,Al,Cr)_2O_3$. The slag is used for vanadium

extraction by chemical methods (as described previously) or for smelting vanadium ferroalloys (Gasik et al., 2009).

The recovery of high vanadium slags from titanomagnetites is also realized by partially reducing vanadium ore with coal in large rotary kilns and then feeding this hot ore into a submerged arc electric smelting furnace. Here slag contains substantial amounts of titania, but the metal is similar to that obtained in blast furnaces. Conversion of the metal to vanadium-rich slag is the same with either the bottom or the top oxygen blowing method (Baroch, 2005).

13.3.3 Reduction of Vanadium from Oxides

Reduction of vanadium is in principle possible via carbon, silicon, and aluminum. Carbon reduction, however, ends up with the formation of high-carbon product due to the strong predilection of vanadium to form carbides (VC). Silicon and aluminum allow the formation of vanadium-rich metal. Aluminum reduction is very exothermic and requires some dummy load components to decrease specific heat generation during the process (Gasik et al., 2009).

13.4 TECHNOLOGY OF FERROVANADIUM

Depending on the content of impurities different ferrovanadium grades are produced (Table 13.3). As described previously, it is possible to obtain ferrovanadium by either silicon or aluminum reduction, and both processes are used commercially.

13.4.1 Reduction by Silicon

Ferrovanadium is produced by the reduction of V_2O_5 by silicon from ferro-silicon in the presence of lime in the electric arc furnace (3 MVA). The technology used for the smelting of ferrovanadium in the electric arc furnace utilizes three periods. The purpose of the first period is to restore vanadium from the current (return) fusion products of the third period of the previous heat. The charge, consisting of a recycled furnace slag, lime flux, ferrosilicon, aluminum, vanadium pentoxide, and iron chips, is loaded (Table 13.4). After the first period (80 to 100 min), V_2O_5 content in the slag is reduced to 0.25% to 0.35%, and the metal ends with 25% to 30% V, 20% to 24% Si, and 0.3% to 0.5% C. The slag with this low content of vanadium is tapped from the furnace.

In the second period, the basic operations are to restore additional V_2O_5 with silicon and aluminum to increase vanadium content in the metal >35% V and to decrease silicon content in the metal below 10% to 12% Si. Here the charge loaded in the second period is composed of vanadium pentoxide, lime, FeSi75, and aluminum (see Table 13.4). After melting, the mixture is stirred to accelerate the recovery of vanadium. At this time, the metal contains 6% to 8%

TABLE 13.3 The Composition of Ferrovandium, % wt. max.*

Grade	V	Si	Al	C	S	P	As	Cu	Mn
FeV75C0.1	70–85	0.8	2	0.1	0.05	0.05	0.05	0.1	0.4
FeV75C0.15	70–85	1	2.5	0.15	0.1	0.1	0.05	0.1	0.6
FeV50C0.4	48–60	1.8	0.2	0.4	0.02	0.07	0.01	0.2	2.7
FeV50C0.5	48–60	2	0.3	0.5	0.02	0.07	0.01	0.2	4
FeV50C0.6	48–60	2	0.3	0.6	0.03	0.07	0.02	0.2	5
FeV50C0.3	>50	2	2.5	0.3	0.1	0.1	0.05	0.2	0.2
FeV50C0.75	>50	2	2.5	0.75	0.1	0.1	0.05	0.2	0.2
FeV40C0.5	35–48	2	0.5	0.5	0.05	0.08	0.03	0.4	2
FeV40C0.75	35–48	2	0.5	0.75	0.05	0.08	0.03	0.4	4
FeV40C1	35–48	2	0.5	1	0.05	0.1	0.03	0.4	6

* The two first grades (FeV75) are produced by aluminum reduction, others by silicon reduction.

Si and the slag contains 8% to 10% V_2O_5 , and ferrosilicon and aluminum are loaded at this stage. When the metal composition reaches 35% to 40% V, 9% to 12% Si, and 0.4% to 0.6% C and the V_2O_5 content in the slag drops to <0.35% V_2O_5 , the second period (~1 h) ends and the slag is tapped.

TABLE 13.4 Consumption of Charge Materials (kg) in the Smelting of Ferrovandium

Materials	Smelting Period			Total
	1	2	3	
V_2O_5 (technical grade 75%)	250	1000	900	2150
Lime	1100	2000	1000	4100
Steel chips	500	—	—	100
Recycled slag of the third period	1932	—	—	—
FeSi75	800	210	—	1010
Aluminum	50	55	—	105
Tapped metal from the previous period	—	1417	1866	—

In the third period (refining; 40 to 60 min) more lime and vanadium pentoxide are added (Table 13.4), and the purpose is to utilize remaining silicon in the metal to reduce more vanadium. The metal is tapped upon reaching $<2\%$ Si into a refractory-lined ladle. The slag from the third period (12% to 16% V_2O_5) is tapped into the skimmer and used in the first period of the next heat. Ferrovanadium is poured from the ladle into vertical cast-iron molds (Gasik et al., 2009).

13.4.2 Technology of Ferrovanadium by Reduction by Aluminum

The aluminothermic process for preparing a ferrovanadium alloy differs from silicon reduction processes in that the reaction is highly exothermic and it allows the production of ferrovanadium with low carbon content (0.02% to 0.06% C). The charge consists of vanadium pentoxide, aluminum powder, steel chips (iron scrap), and lime. The process might be improved with some additions of magnesia. Maximum metal output is achieved when lime content is about 30% to 40% by weight of the vanadium pentoxide amount. The metal contains 82% to 84% V, 1% to 2% Si, $<0.05\%$ P, 0.1% Ti, 1.5% Mn, and slag ends with $<4.5\%$ V_2O_5 . Extraction of vanadium (yield) in the alloy is 90% to 96%.

The vanadium loss with the slag can be reduced by using additional heating at the end of the process. In this case the smelting starts in the furnace (350 kVA) with risen electrodes and proceeds normally without a power supply (Gasik et al., 2009). Upon finishing, the power is turned on and the slag and metal are heated and mixed to improve conditions for the recovery of vanadium and the deposition of metal drops. The dumped slag $<1\%$ V_2O_5 is tapped and the excess aluminum in the metal is reduced by the addition of a controlled amount of V_2O_5 and FeO. If the vanadium content in the slag remains high, it is recycled to the next heat.

Ferrovanadium can also be prepared by the thermite (exothermic) 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 (Baroch, 2005). This method is also used to prepare vanadium master alloys.

13.5 TECHNOLOGY OF OTHER FERROVANADIUM ALLOYS

Ferrosilicovanadium (Table 13.5) is obtained directly from the converter slag in the electric furnace batch process by reducing vanadium with ferrosilicon with lime and fluorspar as fluxes. The process is carried out in a submerged-arc electric furnace with either silicon or carbon (for alloys with $>2.5\%$ C).

For alloying structural steels with vanadium and manganese, FeMnV alloys have been developed (Table 13.6). They are produced similarly to FeSiV, and their costs normalized to 1 kg of vanadium in them is 35% to 40% lower than for standard FeV alloys.

TABLE 13.5 Chemical Composition, % wt. of FeSiV Alloys

Grade	V	Si	Ti	Mn	Cr	C	P	S
			Max.					
FeVSi1	>10	14	3	10	2.5	1.5	0.1	0.03
FeVSi1A	>10	10–20	3	10	4	1.5	0.15	0.03
FeVSi2	>8	20	5	15	4	3	0.2	0.08

TABLE 13.6 Chemical Composition, % wt., of FeMnV Alloys

Grade	Mn	V	C	Si	P	S
			Max.			
FeMnV1	40–50	7–10	2.5	3	0.1	0.005
FeMnV2	45–55	4.5–6	2.5	3	0.1	0.005
FeMnV3	60–65	3–4.5	2.5	3	0.1	0.005
FeMnV4	45–55	4.5–6	6.5	5	0.1	0.005
FeMnV5	60–65	3–4.5	6.5	5	0.1	0.005
FeMnV6	75–78	1.5–2.5	7.5	5	0.1	0.005

13.6 THE TECHNOLOGY OF NITRIDED FERROVANADIUM

Vanadium actively reacts with molecular nitrogen (or other nitrogen-containing substances) above 700°C, forming nitride (VN). It is a refractory nitride (melting point ~2360°C) and an efficient hardener in steels when it forms in situ during thermal treatment (nitride (VN) or carbonitride (V[C,N])). Nitrided ferrovanadium can be obtained in different ways: (1) the solid phase method by saturation of the FeV alloy powder with nitrogen (6% to 8% N) at 900°C, (2) from the melt by blowing with nitrogen (3% to 4% N), and (3) by plasma nitriding (0.3% to 0.5% N). There are also methods of FeVN processing that utilize self-propagating high-temperature synthesis (SHS) on a small scale; nitriding can also be applied to FeSiV alloys.

The addition of nitrided FeV to the steel is accompanied by the dissolution of both vanadium and nitrogen, which recombines upon crystallization of steel ingots and during the subsequent heat treatment.

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