

Technology of Zirconium Ferroalloys

Michael Gasik

Aalto University Foundation, Espoo, Finland

Chapter Outline

16.1 Properties of Zirconium and Its Main Compounds	435	16.3.1 Ferrosilicozirconium	443
16.2 Sources of Zirconium and Its Reduction	441	16.3.2 Technology for Producing Ferro-aluminum-zirconium	446
16.3 Technology of Zirconium Ferroalloys	443	References	447

16.1 PROPERTIES OF ZIRCONIUM AND ITS MAIN COMPOUNDS

Zirconium is an element of group IV of the second great period of transition elements of the periodic system. It has serial number 40, atomic weight 91.22, and an atomic outer electronic configuration of $4d^25s^2$, thus mostly leading to valencies +2 and +4.

Zirconium density at room temperature is 6.49 g/cm^3 , its melting point is 1855°C , and its boiling point is 4350°C (there are also other data estimating that the melting point is $\sim 1860^\circ\text{C}$ and the boiling point is between 4377° and 4409°C). Elementary zirconium exists in two modifications: β -Zr has a body-centered cubic (BCC) lattice with lattice period $a = 0.361 \text{ nm}$ and a density 6.5107 g/cm^3 , and α -Zr has a hexagonal lattice ($a = 0.3231 \text{ nm}$, $c = 0.5146 \text{ nm}$), which is stable at room temperature. The phase transition α -Zr \leftrightarrow β -Zr occurs at 863°C . The molar heat capacity of zirconium is shown in Figure 16.1.

Pure zirconium is a highly reactive metal (analogous to titanium). Its high affinity for oxygen, sulfur, and nitrogen dictates its principal uses in steel-making for the control of nonmetallic inclusions and the fixation of nitrogen

(into ZrN) and to some extent sulfur as well (into ZrS₂). Zirconium also reacts with carbon, forming rather strong carbides (ZrC). In some steels and alloys, zirconium is known to inhibit grain growth and prevent strain aging, giving better isotropy of mechanical properties. As an alloying element (<0.5% Zr) in steels, it improves ductility, strength, wear, and corrosion resistance (Chokalingam et al., 2011).

The manufacturing of pure zirconium requires a combination of complex extractive metallurgical processes, and this makes the pure metal very expensive and supports its application in steelmaking in the form of a ferroalloy (Gasik et al., 2009). The phase equilibria diagrams, which have a practical interest with respect to zirconium alloys, are shown here with iron, carbon, silicon, aluminum, and oxygen.

The system Zr-Fe has a variety of intermetallic compounds: Fe₄Zr (possibly a metastable phase), Zr₃Fe, Zr₂Fe, ZrFe₂, and ZrFe₃, and two eutectic temperatures of ~1337 and 928°C. The most refractory compound is ZrFe₂ (melting point ~1673°C) (Fig. 16.2). It is noteworthy, however, that the exact phase equilibria diagram of this system is not yet well studied and there are some contradictory data in phases existence, composition, and transition temperatures. The presence of metallic and nonmetallic (O, N) impurities may significantly affect the constitution of observed phases.

With carbon, zirconium forms one single stable compound—carbide ZrC (structure of NaCl type) with a melting point of ~3540°C, a density of 6.66 g/cm³, and a wide composition range (36% to 49% at. C). In this system, two eutectic temperatures are 1805 (Zr-ZrC) and 2927°C (ZrC-C) (Fig. 16.3).

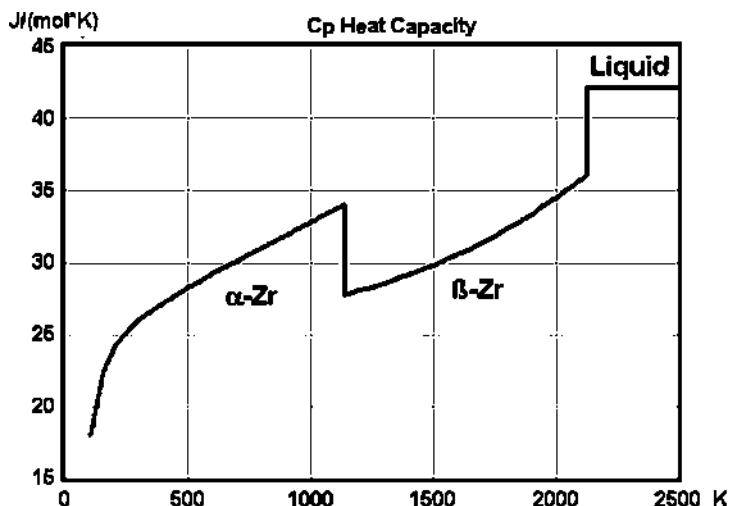


FIGURE 16.1 Molar heat capacity of zirconium versus temperature.

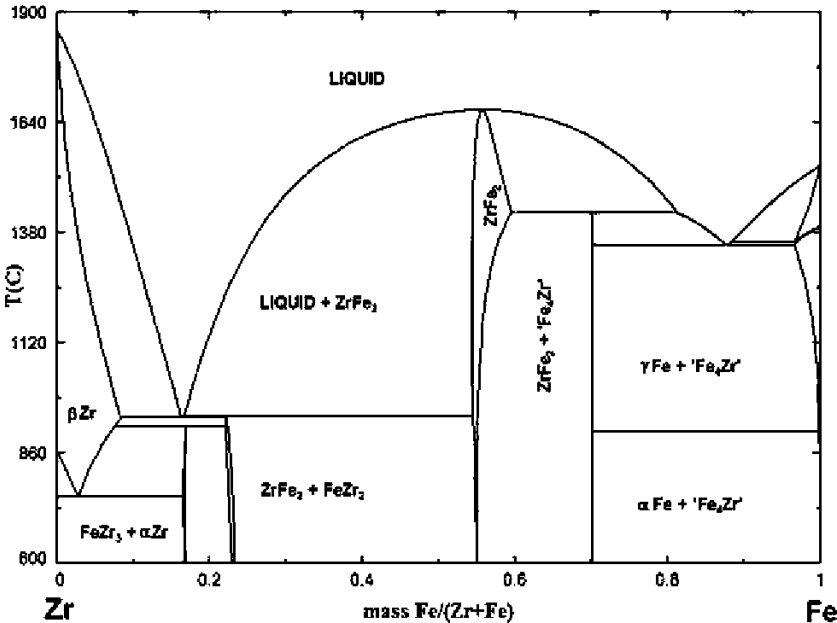


FIGURE 16.2 Zr-Fe phase equilibrium diagram.

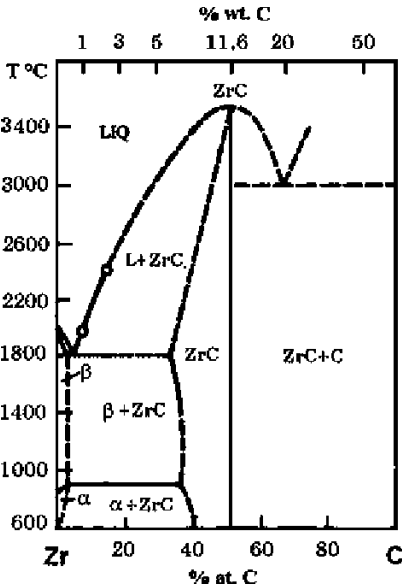


FIGURE 16.3 Zr-C phase equilibrium diagram.

For the Zr-Si system, there are seven known zirconium silicides, and they are commonly considered to be stoichiometric compounds. The most refractory is Zr_5Si_4 , with a melting point of $\sim 2250^\circ\text{C}$. Zirconium dissolves up to 0.2% wt. Si, whereas the solubility of zirconium in silicon is negligible (Fig. 16.4). In this version of the calculated phase diagram, some compounds are not shown (Zr_5Si_4 , Zr_3Si_2) as there are not enough reliable thermodynamic data yet to predict their phase boundaries. Other compounds' existence (like Zr_4Si) is still questionable, as the experimental data might differ depending on the sample preparation method and the purity of materials. For example, impurities stabilize Zr_5Si_3 , which is not stable at room temperature, and which formation suppresses all other silicides. This does not yet allow for the determination of more precise phase reaction temperatures.

Like iron and silicon, there are also many intermetallic compounds that zirconium forms with aluminum (at least 10 compounds have been identified). The maximal solubility of aluminum in α -Zr is 3.7% wt. at 940°C ; in β -Zr it is 9.3% wt. at the eutectic temperature 1350°C (Fig. 16.5). The solubility of zirconium in solid aluminum is negligible. The most refractory compounds in this system are ZrAl_3 , ZrAl_2 , and Zr_3Al_2 with melting points of 1580° , 1645° , and 1595°C , respectively.

In the Zr-O system, the stable oxide of zirconium is ZrO_2 , often referred to as zirconia. It has a well-expressed polymorphism: at room temperature the stable phase α - ZrO_2 has a monocline structure, which transforms into the

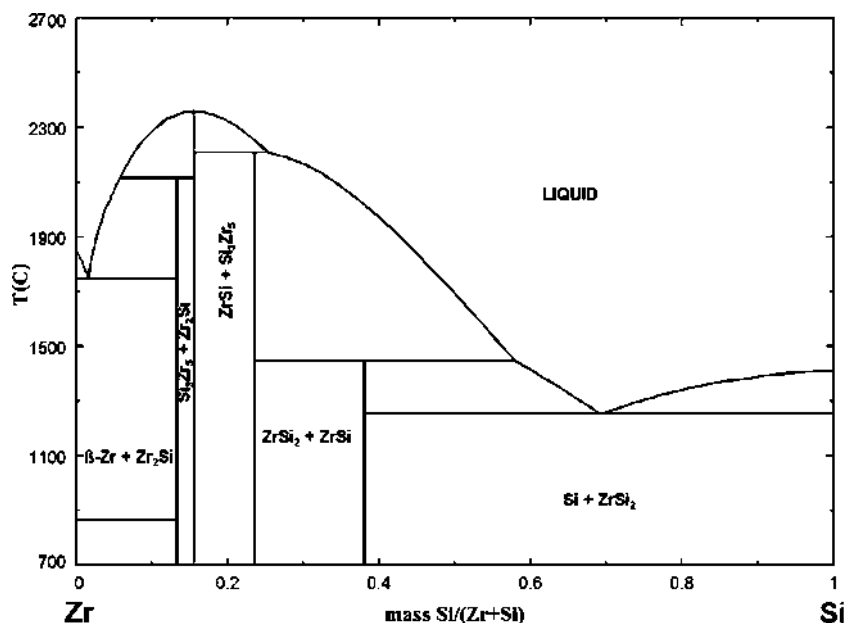


FIGURE 16.4 Zr-Si phase equilibrium diagram.

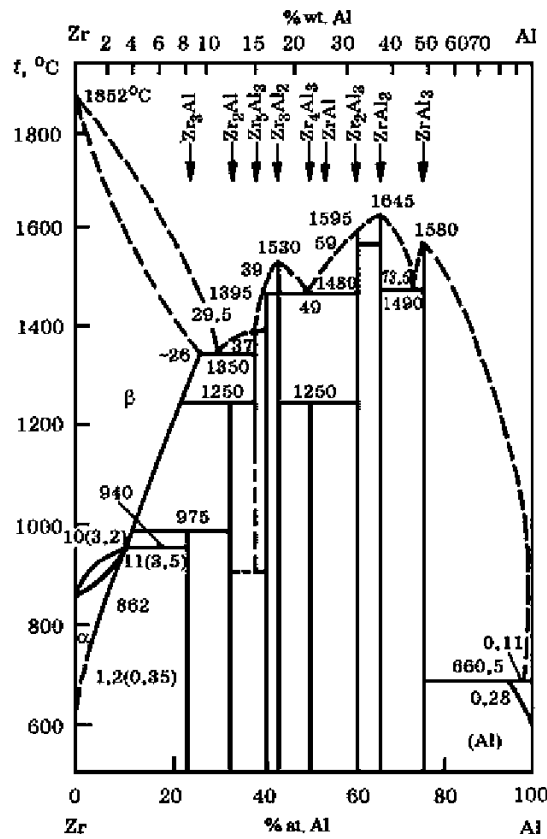


FIGURE 16.5 Zr-Al phase equilibrium diagram.

tetragonal β -ZrO₂ (HgI₂ type) above 1205°C, remaining stable up to 2330°C (Turova, 2011). The phase β -ZrO₂ transforms to the cubic modification γ -ZrO₂ (CaF₂ type) above 2330°C. For the $\alpha \leftrightarrow \beta$ transformation of zirconia, the phenomenon of temperature hysteresis is typical, where the $\alpha \rightarrow \beta$ transition temperature may vary between 1160° and 1190°C (purity-dependent), and the reverse transformation $\beta \rightarrow \alpha$, respectively, between 1070° and 1100°C. The high-temperature reversible transformation $\beta \leftrightarrow \gamma$ at 2330°C has a minimal hysteresis of ~30°C. Impurities such as CaO, MgO, and transition metal oxides may stabilize β and γ phases down to room temperature, which is widely used in the application of zirconia in engineering ceramics. The molar heat capacity of ZrO₂ is shown in Figure 16.6, and the Zr-O phase equilibria are shown in Figure 16.7.

Like titanium, α -Zr may dissolve a substantial amount of oxygen (up to 8.5% wt.) in the solid state, and at low temperatures (<700°C) it tends to form suboxide phases (solutions) of variable compositions (see Fig. 16.7). As noted

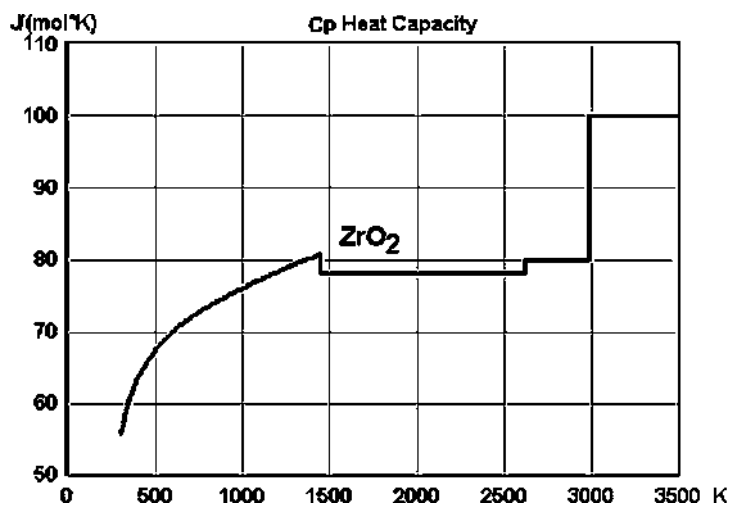


FIGURE 16.6 Molar heat capacity of zirconia.

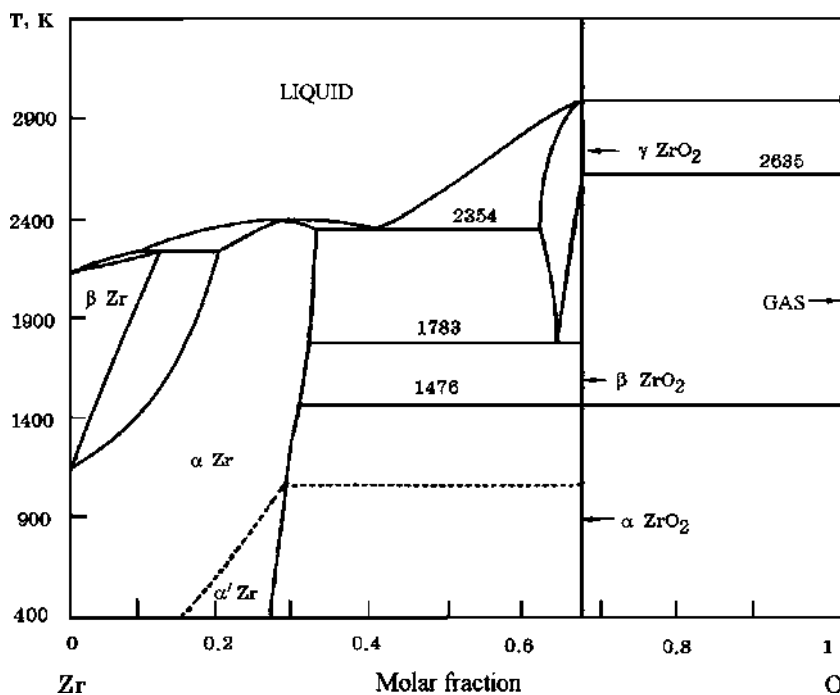
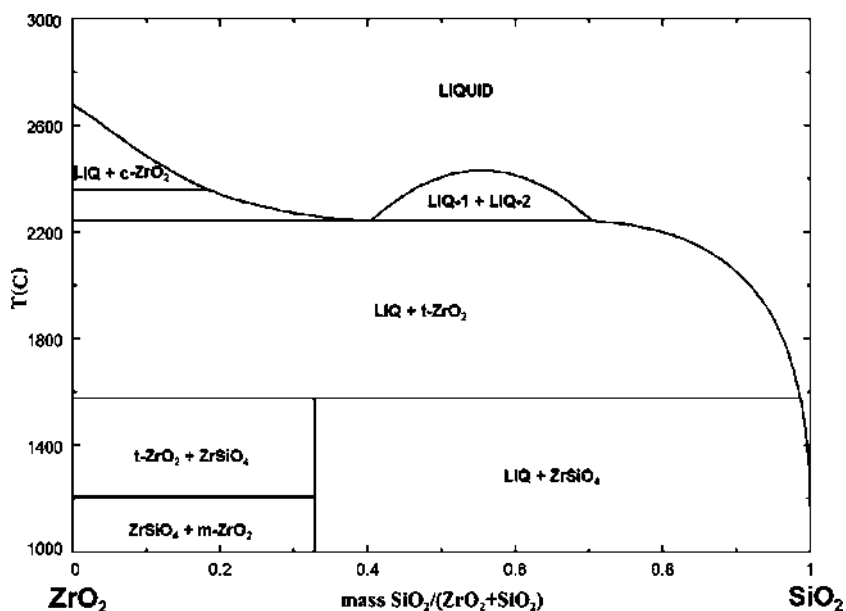


FIGURE 16.7 Zr-O phase equilibrium diagram.

FIGURE 16.8 ZrO_2 - SiO_2 phase equilibrium diagram.

previously, zirconium's high affinity to non-metallic elements restricts the direct application of metallic zirconium in steelmaking or generally at high temperatures in the presence of oxygen, carbon, or nitrogen.

In the system ZrO_2 - SiO_2 , one stable compound $\text{ZrO}_2 \cdot \text{SiO}_2$ (ZrSiO_4) is formed (Fig. 16.8). Zirconium silicate is also the base of the mineral zircon, appearing in nature, in which lattice a number of zirconium sites might be replaced by hafnium and thorium. Zircon usually appears in alluvial deposits, where it associates with other stable minerals. Zirconia and silica practically have no mutual solubility in the solid state, and there is a miscibility gap in the liquid state (42% to 62% wt. SiO_2) over 2250°C.

The phase diagram of the ZrO_2 - Al_2O_3 compound is of a simple eutectic type with an eutectic temperature of 1887°C. This system is important for the manufacturing of alumina-zirconia refractory and abrasive materials.

In the system ZrO_2 - CaO , compounds CaZrO_3 and CaZr_4O_9 , as well as solid solutions of CaO in monoclinic, tetragonal, and cubic ZrO_2 crystal structures are known (Fig. 16.9). CaO , along with yttria and magnesia, is commonly applied to stabilize the cubic phase.

16.2 SOURCES OF ZIRCONIUM AND ITS REDUCTION

Zirconium is a rare element, despite its presence in many minerals, although in small amounts (Hedrick, 2004). The most common minerals of industrial

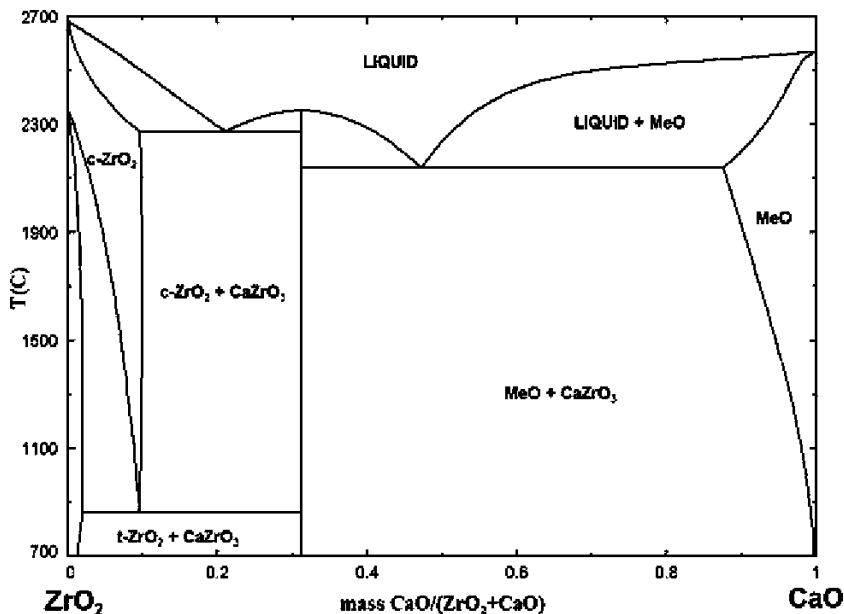


FIGURE 16.9 ZrO_2 -CaO phase equilibrium diagram.

relevance are zircon ($\text{ZrO}_2 \cdot \text{SiO}_2$) and baddeleyite (ZrO_2). Zirconium also forms eudialyte $[\text{Na}_4(\text{Ca}, \text{Ce}, \text{Fe}_2)\text{ZrSi}_6\text{O}_{17}](\text{OH}, \text{Cl}_2)$, which is much less common. Most zircon is mined from placer deposits. Typical zircon concentrates contain 60% to 65% wt. ZrO_2 , <0.1 Fe_2O_3 , <0.4 TiO_2 , <2 Al_2O_3 , <0.1 CaO , <0.1 MgO , <0.15 P_2O_5 , and a balance made up of SiO_2 .

Zirconium can be practically reduced from the concentrates by carbon, silicon, or aluminum. For carbon reduction, as for many other metals, the carbide ZrC is always a reaction product at conventional metallurgical conditions. Figure 16.10 shows the phase dominance (stability) diagram for 1600°C. As the figure shows, the ternary equilibrium point is located at rather low oxygen ($\sim 10^{-21}$ atm O_2) and CO ($\sim 10^{-8}$ atm) potentials, which makes it impossible to reduce ZrO_2 to metallic zirconium here at normal pressure.

Reduction by silicon eventually leads to the formation of zirconium silicides, zirconium intermetallides, and respective melts, forming ferrosilico-zirconium (FeSiZr). As silica is present in zircon concentrates and also is the product of the reactions, the thermodynamics of the reduction process are generally not favorable for getting a high-zirconium-percentage alloy. It would require high temperatures, the addition of basic flux, and an increase of silicon activity, which limits zirconium content to 40% to 45% wt. Therefore, to enhance the process and limit silicon content in the alloy, the reduction is realized by aluminum.

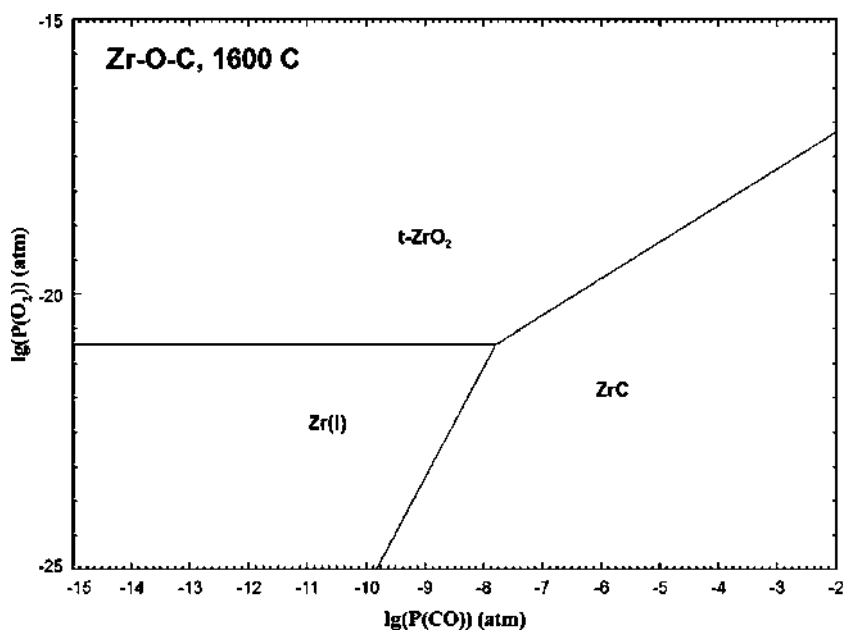


FIGURE 16.10 Zr-O-C phase stability diagram at 1600°C.

Reduction of zirconium by aluminum in the presence of an iron source (exothermic) is used for the production of ferro-alumin-zirconium (FeAlZr) alloy with a low silicon content.

16.3 TECHNOLOGY OF ZIRCONIUM FERROALLOYS

Among the more common zirconium ferroalloys are FeSiZr (average 35% to 40% Zr, 46% to 52% Si), NiZr (67% to 74% Zr, 24% to 30% Ni), FeZr (75% min. Zr), and FeAlZr (15% to 21% Zr, 20% to 26% Al, <4% Si, <0.15% C).

Ferrozirconium, produced by remelting zirconium (zircalloy grades) and steel scrap, may contain between 40% and 90% Zr, depending on the grade, but also low amounts of silicon and aluminum. Nickel–zirconium master alloy is sometimes used as an addition agent in nickel–based superalloys. The technology of FeZr and NiZr relying on scrap remelting, without the reduction of primary materials, is not considered here. The choice of the zirconium alloy depends on the intended application, and for silicon-containing alloys the level of silicon allowed in the steel composition is usually important.

16.3.1 Ferrosilicozirconium

The composition of FeSiZr typically spans from 20% to 45% Zr, with 5% to 9% wt. Al, <0.2% to 0.5% C, <0.15% to 0.20% P, and <3% to Cu. The mass ratio

Si/Zr varies according to the Zr content from 0.5 for high-zirconium grades ($>35\%$ Zr) to ~ 1.7 for the lowest grades (20% to 30% Zr).

The main method used to produce FeSiZr is the reduction of raw materials by aluminum, but it is also possible to use silicon and carbon as reductants. This can be realized in two ways: a flux process and a flux-less process (Gasik et al., 2009). The first option foresees the use of flux (additions of lime and fluorspar) and its main product is the ferroalloy only. The second option involves simultaneously making two products (FeSiZr and zirconium-corundum slag) without fluxing additions. For a proper thermal balance, the charge includes magnetite ore (iron ore with $>60\%$ Fe and low phosphorus, preferably also with $<7\%$ of silica; grain size up to 3 mm). Either primary or secondary aluminum powder is used as a reductant, and it mainly determines the amount of impurities in the final alloy. The one-stage flux process of FeSiZr smelting could be realized either for a tapping of a liquid alloy or for the manufacture of a solid alloy ingot ("block" type). Figure 16.11 shows a schematic of the production of FeSiZr by the flux process with melt tapping. The arc furnace used is typical in steelmaking, of power 1 MVA and carbon-based lining, overlaid with carbon paste. The lining is first fixed and cured by coking it for 8 to 10 h under a normal current and periodically switching off the furnace power.

The charge is calculated for the concentration of zirconium in the alloy as 50% to 54% Zr. The average consumption of charge materials for smelting of 1 ton of FeSiZr using secondary aluminum and with the melt tapping method is 1094 kg of zircon concentrate ($60\% \text{ ZrO}_2$), 543 kg of secondary aluminum

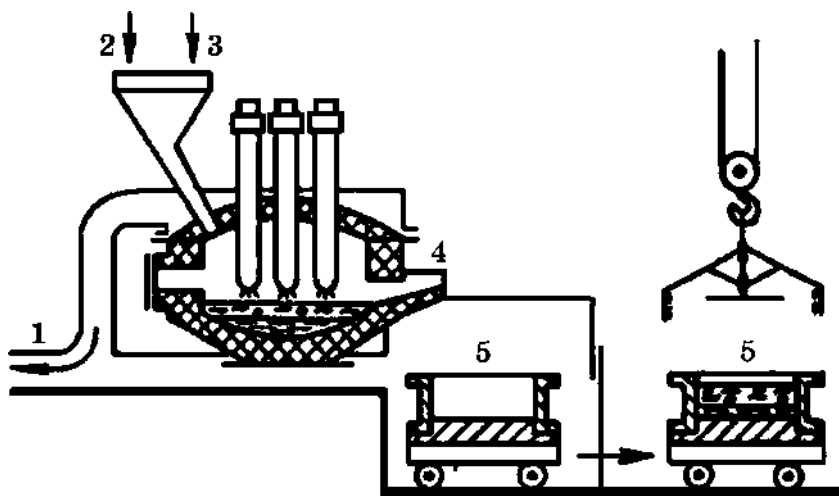


FIGURE 16.11 Schematic of FeSiZr smelting by the flux process: 1, gas exhaust; 2, zircon concentrate feeding; 3, flux and reductant feeding; 4, arc furnace; 5, cast alloy.

powder, 424 kg of lime, 65 kg of ferrosilicon Fe-75%Si, 114 kg of iron ore, and 24 kg of sodium nitrate (used as a reaction initiator). For this kind of smelting, the electricity consumption for 1 ton of the alloy is up to 1500 to 1510 kWh and the zirconium extraction level is 80% to 85%.

The alloy made with this charge typically has 50% to 51% Zr, 26% to 27% Si, 5% to 8% Al, and 0.1% to 0.13% S. The slag composition includes 7% to 9% ZrO_2 , 54% to 56% Al_2O_3 , 28% to 30% CaO, 0.5% to 2.5% SiO_2 , 1.3% to 1.6% MgO, and 0.2% to 0.5% FeO. This method (see Fig. 16.11) allows production of FeSiZr with more than 50% Zr by the simultaneous reduction of Zr and Si by aluminum, but its drawback is that it does not extract zirconium from the oxide melt to a better extent (Gasik et al., 2009).

To improve the zirconium utilization, the simultaneous smelting of FeSiZr and zirconia–corundum ($\text{ZrO}_2\text{--Al}_2\text{O}_3$ material used in abrasive and refractory products) is also used. Flux (lime) is not used in this case, whereas the zirconium-rich slag becomes a commercial by-product (20% to 35% ZrO_2 , <3 SiO_2 , <2 CaO, <2 MgO, and the balance made up of Al_2O_3). The smelting batch of this flux-less process of total weight 2100 to 2400 kg includes zircon concentrate (~1250 kg), secondary aluminum powder (~500 to 630 kg), ferrosilicon (<150 kg), and iron ore (~250 kg). Charge materials must contain a minimum amount of calcium and magnesium oxides, as they represent a decreasing quality of fused zirconia–corundum abrasive products (reducing hardness and cutting ability). The composition of the charge is determined by the fused zirconia–corundum grade required: by decreasing the amount of aluminum powder, the degree of zirconium reduction is decreased and zirconium content increases in the oxide melt.

Melting is performed in an electric furnace of the steelmaking type with a carbon lining. After melting of approximately two thirds of the charge, the fused oxide mixture (slag) is poured into a metal mold. When the melting stage has completed, the rest of the slag is tapped at the bottom of another mold and after it cools down (~3 min), the metal is tapped onto the slag. Per such batch composition, 500 to 600 kg of FeSiZr alloy (40% to 50% wt. Zr, 25% to 35% Si) and 1300 to 1400 kg of zirconium–corundum (25% to 40% ZrO_2) are typically obtained.

The technology for producing zirconium–corundum together with FeSiZr is more effective than for the flux process because here there are practically no zirconium losses. However, the total economic efficiency of the process also depends in this case on the market situation for both the metal and the ceramic materials (by-products), and they may not always be simultaneously correlated.

In the case of the silicon reduction method, the charge consists of zircon concentrate, FeSi75, and lime. This FeSiZr alloy naturally has a higher silicon content (47% to 50% Si) and a lower zirconium content (33% to 37% Zr). The advantages of this alloy are a better utilization of zirconium in steelmaking and the simultaneous addition of silicon to molten steel, decreasing the need for extra additions of FeSi.

In the case of the carbon reduction method, charcoal is also added to the charge and the resulting alloy has 15% to 18% Zr, 36% to 40% Si, <1% Al, and <0.5% C. It is possible to produce FeSiZr with higher zirconium content, but it comes at the expense of the increased silicon percentage. The selection of the reduction method in that case is based on the whole set of technical and economic conditions.

16.3.2 Technology for Producing Ferro-aluminum-zirconium

The composition of ferro-aluminum-zirconium usually includes 15% to 20% Zr, 15% to 30% Al, and balance – Fe; the main impurity is silicon (<3%). Due to the limitation of silicon content, zircon ZrSiO_4 cannot be used as a raw material and the zirconium source is mainly zirconia concentrate (baddeleyite). Iron is added in the form of iron ore pellets and iron scale. The reductant is aluminum powder in the presence of lime as flux. For ignition of the charge, sodium nitrate is also added. Table 16.1 gives an example of the charge: it consists of three types: for ignition, for zirconium reduction, and for exothermal generation.

This process has a complex set of physicochemical interactions. First, the ignition charge gives a necessary thermal impulse for the whole process of initiation. It is based on the very exothermic reaction (-1250 kJ/mol of sodium nitrate):

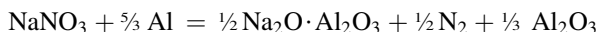
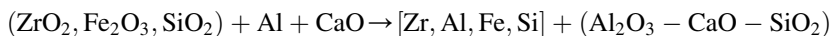


TABLE 16.1 Composition of Charge for Making Fe-18% Al to 22% Zr Alloy

Charge Components	Amount, kg			Total
	For Ignition	For Ore Reduction	For Exothermal Part	
Zirconia ZrO_2	—	480	—	480
Zircon ZrSiO_4	150	—	—	150
Iron scale	20	400	180	600
Iron pellets	—	200	—	200
NaNO_3	35	—	—	35
Lime	40	350	100	490
Al powder	90	590	80	760
Total, kg	335	2050	360	2715

The main reduction process involves the formation of the metallic melt, and it is a summary product of many reactions that might be presented schematically as follows:



At the final stage, the process is accelerated by feeding the exothermic mixture (iron oxide, lime, and aluminum powder) into the bath of the furnace. This is supposed to cause extra local heating and finalization of the reduction and the slag formation. Zirconium extraction in this process is nevertheless only 45% to 50%.

Different kinds of more complex master alloys with zirconium are also being produced. They may also contain manganese, aluminum, silicon, and titanium, with less zirconium (10% to 15%)—for example, the FeSiZrMn alloy may have 4% to 22% Zr, 4% to 15% Mn, and 45% to 67% Si, which could be complemented by 3% to 9% REM and <15% Ti on request.

REFERENCES

- Chokkalingam, B., Mohamed Nazirudeen, S.S., Ramakrishnan, S.S., 2011. Investigation into the mechanical properties of micro-alloyed as-cast steel. *Materials and Technology* 45, 159–162.
- Gasik, M.I., Lyakishev, N.P., Gasik, M.M., 2009. *Physical Chemistry and Technology of Ferroalloys* [in Ukrainian]. Sistemnye Tehnologii, Dnipropetrovsk, 494 pp.
- Hedrick, J.B., 2004. Zirconium and hafnium. *U.S. Geological Survey Minerals Yearbook*, 85, 1–11.
- Turova, N., 2011. Titanium, zirconium, hafnium. In: *Inorganic chemistry in tables*. Springer, Berlin-Heidelberg, pp. 66–67.