

Zirconium facts at your fingertips

Zirconium, the chemical element with the symbol Zr is a lustrous gray-white, strong transition metal that resembles titanium. Due to its high resistance to corrosion it is often used as an alloying agent. As a metal, it is never found in the earth's crust in pure form but instead occurs mainly as a zirconium silicate ($ZrSiO_4$), found primarily in Australia, Brazil, India, Russia, South Africa and the United States. In this article many of the properties and characteristics of zirconium are highlighted.

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Thanks to the Kroll process, metallic zirconium can be produced by means of a fairly complicated reduction process. In actual fact, the ore is found as a by-product when mining titanium and tin ore. Since 2003, the price of zirconium has more than doubled. This is the result of increasing demand and also the fact that a considerable amount of energy is needed to release zirconium from its chemical bond. Chlorination is performed to convert zirconium ore into the tetravalent zirconium chloride. This compound is then reduced with magnesium to produce metallic zirconium and magnesium chloride. All in all, this is a very energy intensive process, just as with the metal titanium. 1 to 3% hafnium is also produced as a by-product. Zirconium is classed as a reactive metal because it forms a solid and compact layer of zirconium oxide on the surface without electrolyte. Zirconium is often thought to be a precious metal because it behaves very much like one but this is not the case. The oxide layer is noble and very stable, providing the underlying metal with optimum protection against all kinds of chemical reagents. In this area, zirconium is superior to its sister metal titanium, especially at increased

temperatures. This is chiefly manifested in the preparation of nitric acid, in which zirconium offers extreme resistance against corrosion, even with the presence of chlorides. Zirconium also allows process temperatures to be

increased without problem to enable a more efficient way of working. Table 1 shows the chemical composition of the most common commercial zirconium grades.

Table 1: Chemical composition of zirconium and zirconium alloys.

Zirconium 702 is considered to be the only technically pure zirconium grade on the market. It can also be said that this is effectively a non-alloyed grade. Table 2 shows the physical properties of zirconium and zirconium alloys and Table 3 the mechanical values. What is particularly noticeable in Table 3 is the substantial increase in the elastic limit and tensile strength the higher the alloy content of the material, while the elasticity remains almost constant. The main reason for the modest elasticity value is the material's hexagonal atomic structure, which, by definition, has a limited number of glide planes.

Chemical composition (%)	Zirconium grade with UNS number			
	Zr 702 R60702	Zr704 R60704	Zr705 R60705	Zr706 R60706
Zr+Hf	99.2	97.5	95.5	95.5
Hf maximum	4.5	4.5	4.5	4.5
Fe+Cr	<=0.2	0.2-0.4	<=0.2	<=0.2
Sn	-	0.1-2.0	-	-
H	0.005	0.005	0.005	0.005
N	0.025	0.025	0.025	0.025
C	0.05	0.05	0.05	0.05
Nb	-	-	2.0-3.0	2.0-3.0
O	0.16	0.18	0.18	0.16

Table 2: Physical properties of non-alloyed and alloyed zirconium.

Physical properties	Zirconium 702	Zirconium 705
Atomic number	40	-
Atomic weight	91.22	-
Specific weight	6.51	6.64
Crystal structure (α phase)	Hexagonal <865°C	-
Crystal structure (β phase)	--	Body-centred cubic >854°C
Crystal structure (α + β phases)	Body-centred cubic >865°C	Hexagonal + body-centred cubic < 854°C
Melting point °C	1852	
Boiling point °C	4377	1840
Coefficient of expansion at 20°C	5.98, 10 ⁻⁶	4380
Thermal conductivity in W/moK (between 300-800°K)	13	6.3, 10 ⁻⁶
Electrical resistance at 20°C in micro-ohm.cm	39.7	10
		55

Table 3: The mechanical values of zirconium and zirconium alloys.

Grade	Zr 702	Zr704	Zr705	Zr706
Tensile strength in MPa	379	411	552	510
Elastic limit 0.2% in MPa	207	241	379	345
Elasticity in %	16	14	16	20



Fig. 1. Zirconium fuel rods for the nuclear industry.

Below 865°C, zirconium has a hexagonal packing structure (α -phase) which transforms into a body-centred cubic structure (β phase) above this temperature. It is impossible to obtain this β -phase at room temperature with any type of heat treatment. Due to the hexagonal structure, the atomic lattices only have two glide planes, which means that zirconium, just like tita-

niun, is not easy to deform. Dopants have a significantly positive influence on the mechanical values of zirconium.

Alloying elements

Alloying elements are able to promote the formation of the α -phase or the β -phase. These are therefore also known as α - or β -stabilizers. Elements

that promote the α -phase include aluminium, antimony, tin, beryllium, hafnium, nitrogen, oxygen and cadmium. Stabilizers that promote the β -phase include iron, chromium, nickel, molybdenum, copper, niobium, tantalum, vanadium, uranium, titanium, manganese, cobalt and silver. Due to the hexagonal structure, values such as the expansion coefficient, tensile strength, elasticity and bending strength vary depending on the orientation of the crystal lattice.

Zirconium in nitric acid

Stainless steel types AISI 316 and 304 have always performed particularly well in the preparation of nitric acid within certain process conditions. If the concentration or temperature became too high, the limitations started to become visible and a higher chromium alloy was applied or the wall thickness was reinforced significantly. Allowing the molybdenum content to increase appears to have hardly any positive effect on the performance of the austenitic stainless steel. Despite various measures, the lifespan of this type of equipment appears to be limited as the stainless steel proves to be susceptible to crevice and stress corrosion in environments in which chlorides are also present in the nitric acid. It therefore quickly became apparent that titanium would be a better alternative. However, zirconium does appear to be the ultimate material to use in the preparation of nitric acid. With acid concentrations below 70% and temperatures below 260°C, the corrosion rate turns out to be no greater than 2.5 μm per year and this is extremely low. The potential of the passive zirconium oxide layer is consider-

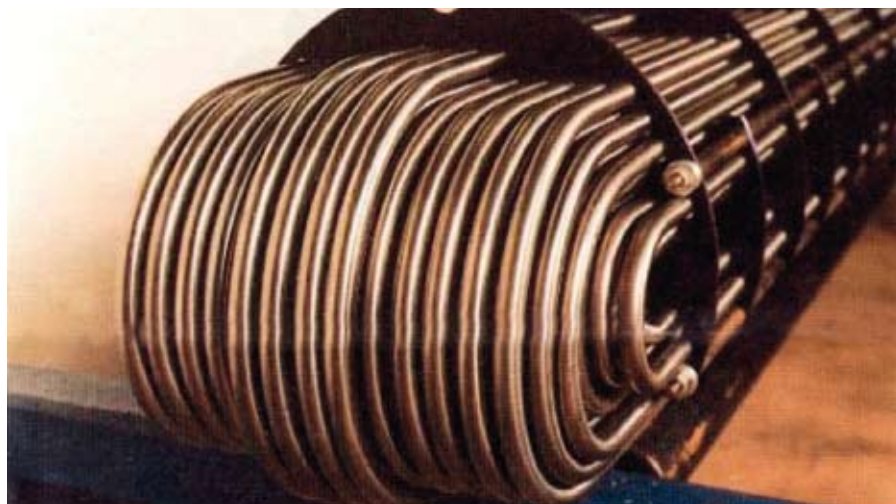


Fig. 2. Zirconium 702 heat exchanger (photo Wah Chang).

ably higher than that of stainless steel. This is why even aggressive dopants such as ferric chloride and hexavalent chromium ions have no adverse influence on the corrosion performance of zirconium in hot nitric acid.

Summarising, zirconium in nitric acid is not susceptible to all kinds of variations in acid concentration, the degree of purity, temperature and the condition in which the nitric acid is found. If, however, the acid concentration is higher than 70%, there is a small risk of stress corrosion, which can be completely eliminated by first stress-relieving the material by annealing it at 565°C for half an hour to an hour. However, the construction must be designed in such a way that no high mechanical tensions can develop. In general, pickling must be carried out after annealing and this can best be done in a solution of 25 to 50% nitric acid, 3 to 7% hydrogen fluoride and the rest water. To prevent hydrogen absorption during pickling, the ratio between nitric acid and hydrogen fluoride must be at least 10 to 1. After pickling, the products must be rinsed thoroughly.

Another danger is the formation of possible pitting corrosion as soon as zirconium is placed in the vapour phase of nitric acid in which chlorides are also present. The reason for this is the oxidation of chlorides, which leads to the development of chlorine gas that can initiate pitting corrosion. However, if the zirconium surface is in good condition because of adequate pickling, then the risk appears to be extremely small. Certain concentrations of fluoride ions in nitric acid can also pose a corrosion threat but this can then be combated by adding zirconium

nitrate to this medium because this binds the fluorides.

Machining zirconium

In principle, zirconium can be machined effectively providing the following parameters are observed properly - high feed rates, low cutting speeds and copious use of a cutting oil emulsion. This is mainly due to zirconium's tendency to quickly work harden, which is why higher than normal clearance angles on cutting tools are needed. This allows deeper penetration of a cutter in the hardened layer.

Storing zirconium residues requires extra attention because the reactivity of zirconium makes it extremely combustible with a certain ratio between surface area and volume. Combustion releases a huge amount of energy, which makes it virtually impossible, practically speaking, for oxidation to be stopped. It is therefore fairly easy for tiny particles, such as grinding dust and fine chips, to spontaneously combust. This is why such residues must be stored responsibly, which means always under water.

Zirconium lends itself well to welding and, in itself, can even be a fairly simple process if the correct welding parameters are used. Just as with titanium, it is very important that not only the weld zone but also the cooling metal is protected against oxygen penetration. Above 400°C, oxygen can easily penetrate the surface and lead to embrittlement of the zirconium and this is why a trailing shield must be fitted behind the welding torch to protect the material with the use of an inert gas.

Zirconium is mostly welded using the TIG or MIF welding process. In some



Fig. 4. Zirconium fittings.

cases, it can also be done using plasma or electron beam welding. Laser welding is also a good alternative. Zirconium is not toxic, which facilitates the welding process.

Thanks to the low rate of thermal expansion, deformations and tensions are not a great problem during welding. It is very important, however, that the metal is degreased properly and thoroughly cleaned beforehand. Zirconium can only be welded to a few other metals - titanium, vanadium and niobium. Zirconium can, however, be welded to stainless steel or carbon steel by means of explosive welding and examples include tube plates or plates that are rolled after the explosive welding process to be used in reactor vessels. If zirconium needs to be welded to carbon steel thermally, then this is only possible if a layer of vanadium is first welded to the steel. The zirconium can then be welded to the vanadium, but this does require the necessary expertise.

Applications

Zirconium proves to be a versatile metal that is mainly used in the chemical and nuclear sectors. As mentioned earlier, it is found to function particularly well in the handling and recycling of nitric acid, but is also used with success in the preparation of ammonium nitrate and many organic acids. In the nuclear sector, it is especially used as an encasement for the nuclear rods because the thermal neutron absorption is found to be so low.

Its excellent corrosion resistance means it can be used for a wide range of applications in the chemical industry and the iso-corrosion curves below show how well the material performs under various aggressive conditions. The cor-

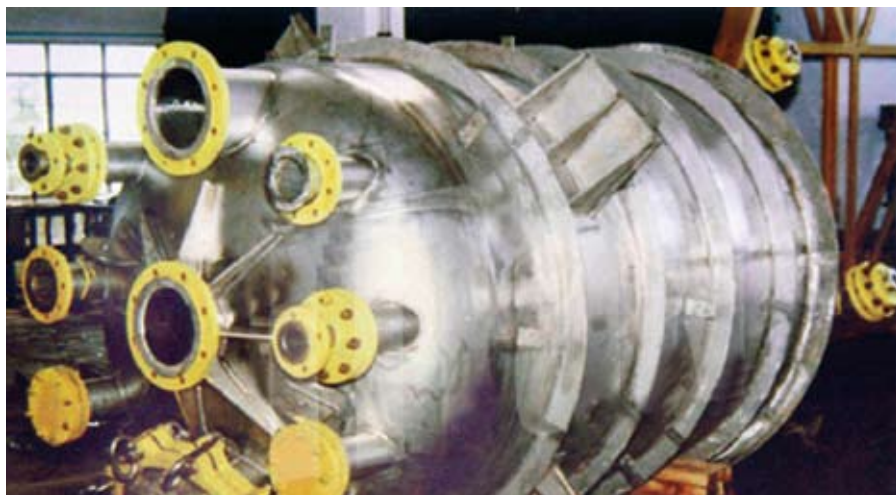


Fig. 3. Zirconium reactor vessel.

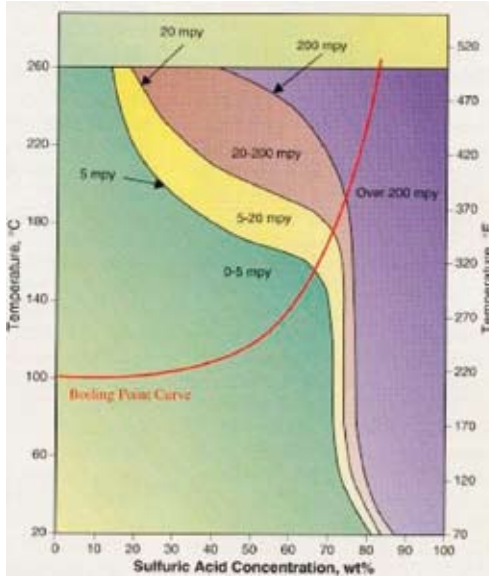


Fig. 5. Iso-corrosion curve of zirconium 702 in sulphuric acid (source Wah Chang).

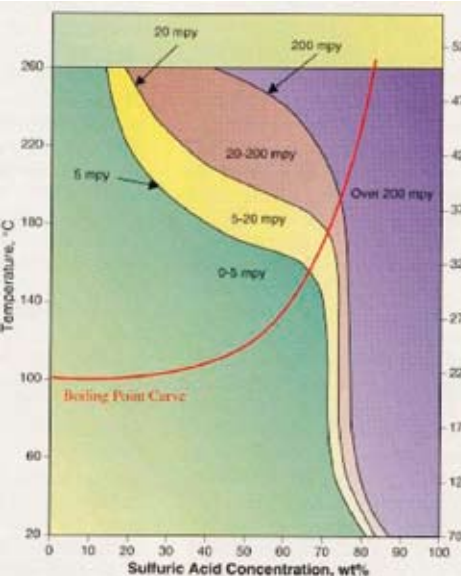


Fig. 6. Iso-corrosion curve of zirconium 702 in hydrochloric acid (source Wah Chang).

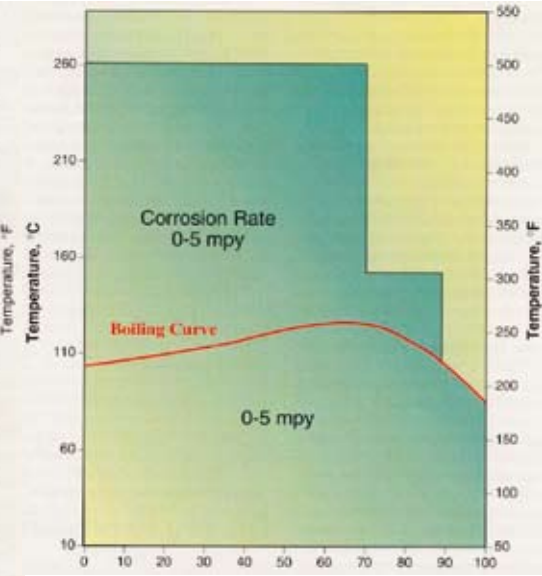


Fig. 7. Iso-corrosion curve of zirconium 702 in nitric acid (source Wah Chang).

rosion rate is expressed in mpy, which stands for “mill per year”. A mill is a thousandth of an inch and the value shown in the tables below is therefore the penetration depth of corrosion per year.

Figure 5 shows the corrosion rate in sulphuric acid as a function of the concentration and temperature. Compared to stainless steel, for example, this resistance is exceptionally high. This also applies when zirconium is exposed to hydrochloric acid (figure 6). As mentioned earlier, zirconium is also a good choice in the preparation and processing of nitric acid (figure 7). It is also possible to cast zirconium, which is why it is used to cast parts such as pump casing (figure 8), impel-



Fig. 8. Cast zirconium pump casing with impeller.

lers, valve boxes etc. Casting does require special attention in connection with the high reactivity of the material. It is therefore relevant to say that zirconium casting is a relatively uncommon activity.

Coloured

Zirconium can also be coloured and this is done using atomic oxygen that thickens the oxide layer to some degree. The oxide layer is naturally transparent and colourless and thickening of this layer produces a different refractive index as a result of which all colours of the rainbow can be obtained (prism effect). In other words, it has nothing to do with the application of a coating as is often thought, but with a natural thickening. This property is of particular importance when jewellery or glasses frames are made from zirconium as shown in Figure 9. This colouring process has no further significance for industrial applications.

Conclusion

Zirconium is a versatile metal that is used with much success, not only in the nuclear sector, but also in the chemical industry. Examples include use in organic and inorganic conditions as well as in strong alkaline environments. Zirconium also produces excellent results in many molten salts, as a result of which it can also replace graphite heat exchangers to a large extent. Although zirconium is not cheap, its use has nevertheless resulted in costs being spared as fewer stop-

pages are needed and less maintenance is required. As no corrosion allowance is needed, material can be spared and this promotes the transfer of heat. Thanks to the hard oxide layer, fluid speeds can also be increased, which leads to better efficiency. Just as with titanium, the hard oxide layer promotes a teardrop-shaped condensation, which improves the efficiency of heat exchangers and condensers. Thanks to the low thermal expansion, there is less risk of thermal fatigue of appliances that need to be suitable for thermal load cycling. In short, zirconium is a unique material whose specific weight lies between that of titanium and stainless steel.



Fig. 9. Coloured zirconium jewellery.

Acknowledgement

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