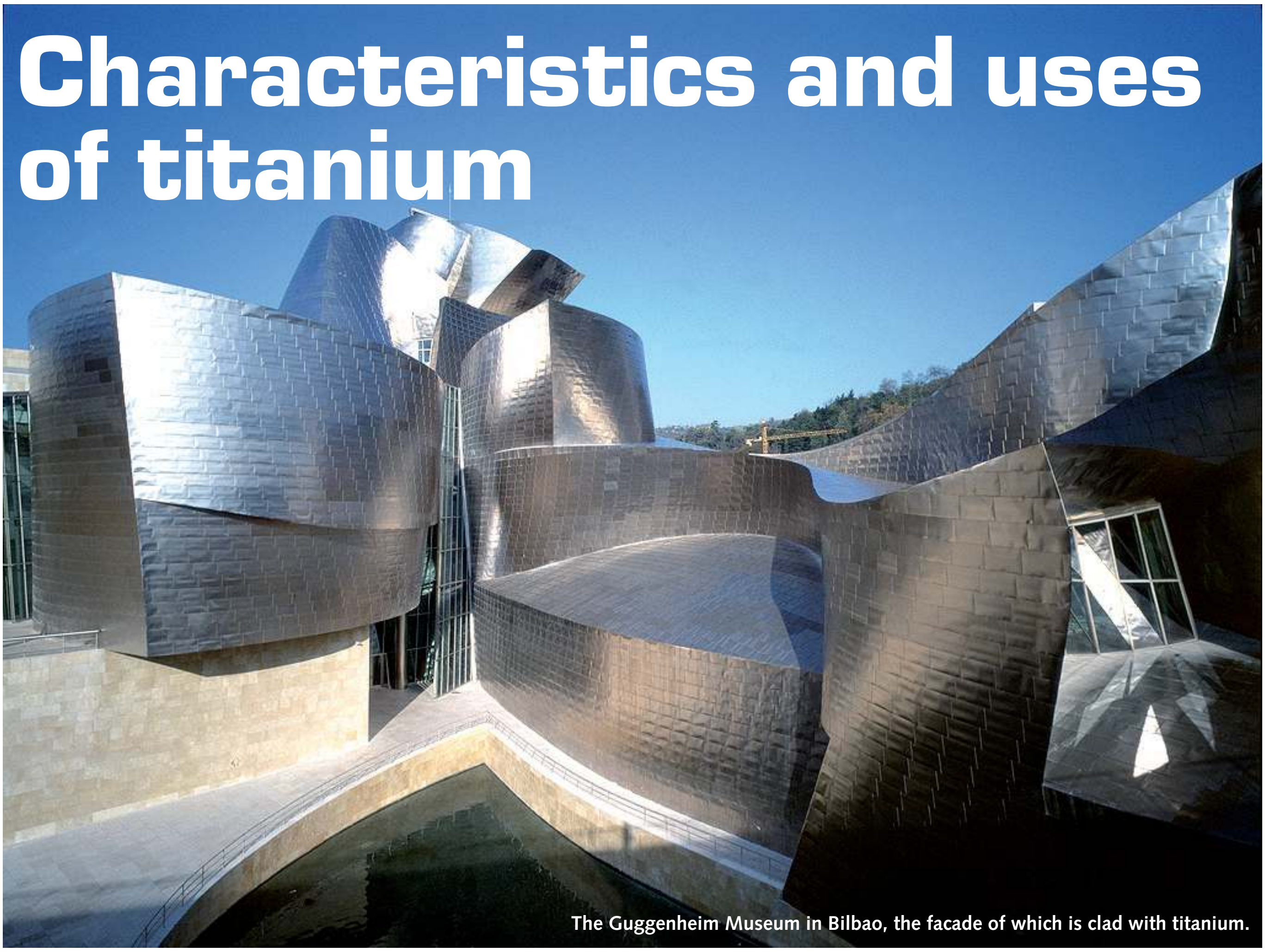
Characteristics and uses of titanium



The Guggenheim Museum in Bilbao, the facade of which is clad with titanium.

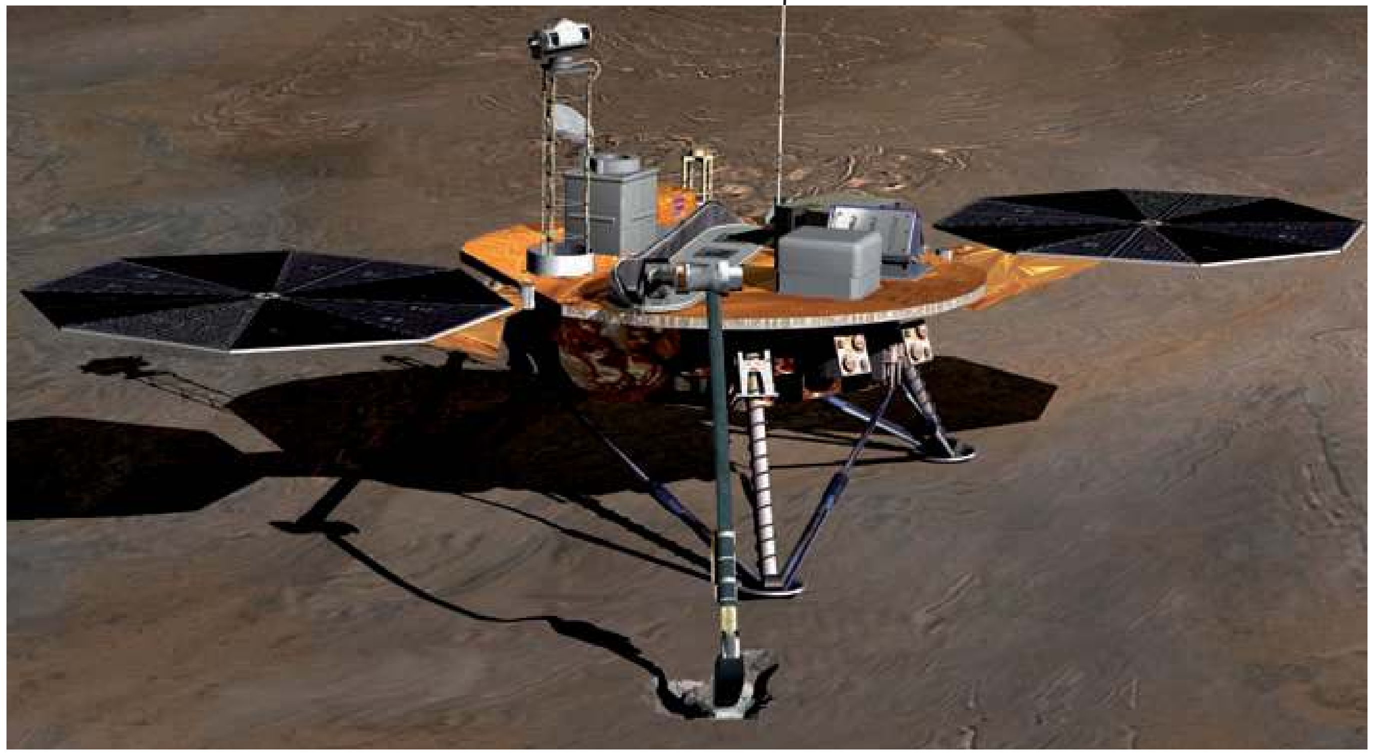
Titanium is an exceptional metal in almost every way: expensive and energy-intensive to produce, highly reactive and uniquely corrosion-resistant. Ko Buijs discusses the characteristics of this metal and provides a summary of some of the leading titanium alloys, including the remarkable shape memory alloys, which can "remember" their original shape.

Ko Buijs, Van Leeuwen Stainless

Obtaining titanium from ore

Titanium is a remarkable, very light metal with a silvery colour and is the fourth most abundant element in the earth's crust. We may therefore ask the question, why is this metal so expensive? To a great extent, the answer lies in the costs involved in obtaining it. As a rule, all ignoble metals are extracted as a metal oxide. The lower the position of the standard potential of the metal in the nobility table, the more difficult it becomes to separate the metal from the bound oxygen. Iron has a potential of -0.44 volts and can be quite easily separated from the bound oxygen. This can be represented by the reduction formula $2FeO + C + e \rightarrow 2Fe + CO_2$. This reaction takes place in a blast furnace, and the "e" in the formula stands for the energy that needs to be added to make this reduction possible. If one adapts this mechanism to titanium oxide, also called rutile, nothing happens, since titanium oxide must be treated very differently in order to separate these two strongly bound elements. This process is as follows:

1. Rutile (TiO2) is chlorinated with cokes to produce titanium tetrachloride (TiCl4) and carbon dioxide (CO2). Titanium tetrachloride is a colourless liquid that remains to be refined.
2. Magnesium or sodium is added to the titanium tetrachloride in an inert environment.
3. This produces the chemical reaction TiCl4 + 2Mg → Ti + 2MgCl2. Finally, we obtain titanium sponge and magnesium chloride.
4. The titanium sponge is pressed into blocks and melted under inert gas to form ingots, to which alloy elements and scrap may be added. These ingots are then rolled to produce all kinds of half-finished products such as sheets or rods.



In this artist's rendition, the Phoenix Mars Lander is shown on the arctic plains of Mars just as it has begun to dig a trench through the upper soil layer. The polar water ice cap is shown in the far distance. This rendition of the Lander was created by artist Corby Waste of the Jet Propulsion Laboratory.

It will by now be clear that it takes a lot of energy to win titanium from its ore. This has to do with the fact that it takes a lot of energy to prepare magnesium or sodium. Therefore a large part of the price of titanium is determined by energy prices.

Characteristics

Titanium is a reactive metal with a standard potential of -1.63 volts, roughly four times more negative than the negative potential of iron. Yet this very ignoble metal behaves in a very noble way in that the titanium dioxide skin provides such excellent protection. Titanium is so reactive that a titanium oxide skin forms spontaneously in contact with air, without the presence of water. By contrast, iron needs moisture as well as air in order to oxidise. Thus iron is an active rather than a reactive metal.

Physical properties of titanium

Melting point	1660°C
Density	4.51
Co-efficient of expansion	8.9 x 10-6/°C
Electrical resistivity at 20°C	48.2 micro-ohms per cm
Standard potential	-1.63 volts
Elastic modulus	105,000 N/mm²

The general properties of titanium can be summarised as follows:

- Relatively low density
- High corrosion resistance
- Good erosion resistance
- Good heat conductivity
- Favourable strength/w eight ratio
- Low thermal expansion
- Aesthetically pleasing appearance
- Hard smooth oxide skin

This last property strongly inhibits the accumulation of dirt and encourages condensation to form in drops, an important factor in the efficient functioning of condensers and heat exchangers. Qualities such as low density, good mechanical characteristics and corrosion resistance are important factors that will quickly justify the use of titanium. In the last 50 years titanium has proved an especially good choice of material in saline, brackish and dirty water. More than 150 million metres of condenser tubes, which are guaranteed for a period of as much as 40 years, have been installed world-wide in electricity power plants, without any degradation having been observed. Originally fire-fighting equipment and cooling systems on offshore platforms were made with carbon steel protected by various kinds of coatings. Because of the damage sustained by these coatings, this material was quickly replaced by cupronickel, but this led to pitting corrosion and erosion (especially in bends) in dirty water. Some designers then tried to overcome these problems by increasing wall thicknesses and lowering water speeds. This led to a slower flow rate, the negative consequences of which were larger pipes diameters, wider bend angles and a large increase in the cost and weight of pipe systems, which also took up more space. Despite all the steps taken, in the long run the various shortcomings resurfaced, and it became apparent that a radical change of course in terms of material choice and a new approach to material design were necessary. More recent designs require not only cost and weight savings but also extremely reliable materials that make it possible to move liquids at higher speeds through tubes with relatively small diameters. To start with, austenitic stainless steels with around 6 per cent molybdenum such as 254SMO were favoured, but later it was super duplex stainless grades that received more attention because of their better performance. Both grades offered more than cupronikkel but were still unable to deliver the desired results and, moreover, presented the inevitable difficulties during fabrication. The extraordinary and unique corrosion performance of titanium offered new perspectives for these applications. It was therefore not surprising that titanium is nowadays chosen very frequently for the fabrication of seawater-cooled heat exchangers and piping systems, and as a condenser material in electricity power stations and various kinds of equipment on ships, such as for example handling systems. Up to now it has turned out that applying titanium guarantees an effective solution to corrosion problems in certain environments. Titanium should in principle always be considered, in both onshore and offshore environments, whenever chloride-containing environments, sulphur compounds or hydrocarbon compounds are present. The financial advantages have already been proved in practice, and the design and fabrication parameters have been adequately established.

Mike Williams, a Lead Mechanical Engineer at the University of Arizona Lunar Planetary Lab, shown installing the structural manifold made of ATI 425® titanium on the Thermal Gas Evolved Analyzer (TEGA). TEGA is one of the instruments installed on the Phoenix Mars Lander. One of the key tasks assigned the Lander is to help determine whether microbial life ever existed on Mars.

Applications

Titanium is used in many applications in the construction of industrial equipment such as in heat exchangers or piping systems in the chemicals and offshore industries, and also in process instrumentation such as pumps and valves. The material can also be found in aircraft construction, medical implants, sports goods such as tennis rackets and golf clubs, spectacle frames, jewellery, paint pigmentation, paper and so on. Well-known applications also include chlorine preparation (membrane electrolysis) and the manufacture of PTA.

Corrosion allowance

One of titanium's most interesting characteristics is that it needs no corrosion allowance. To a great extent, this compensates for its inferior heat conductivity.
With the following formula it is possible to calculate the wall thickness of tubing materials:

$$T_m = \frac{P.D}{2(\sigma + P.Y)} + A$$

T_m = minimum wall thickness (in mm)
P = system pressure (in Mpa)
D = external diameter (in mm)
σ = maximum allowable tension in the design temperature (in Mpa)
Y = a co-efficient
A = corrosion allowance (for titanium, this is 0).

Titanium and titanium alloys

Commercially pure titanium grades are unalloyed, but the degree of the impurity varies from one grade to another. Grades 1 to 4, for example, have an ascending order of impurity. Grade 1, because of its low impurity, the most ductile and therefore is suitable for explosive cladding. Grade 2 is the most common grade while grade 4 has the best mechanical values of the four grades, so as a rule it is used to make fasteners. All these grades belong to the category of α [let op! griekse letters] (alpha) alloys, as do grades 11 and 7, which can be described as grades 1 and 2 to which about 0.2% palladium has been added. This addition of palladium ensures that resistance to crevice corrosion is increased, for instance in warm seawater.
Besides these there are β (beta) alloys and α+β alloys. These are the grades with the highest mechanical values. As a rule they are used in forging alloys and casting alloys. There are many interesting titanium alloys, but space does not permit me to discuss them all here. I will therefore restrict myself to the best-known titanium alloy, grade 5 (Ti-$6Al4V$), which contains 6% aluminium en 4% vanadium. This grade, called the workhorse among titanium alloys, is frequently used in aerospace because of its favourable weight/strength ratio, for the most part in critical components such as the moving parts in wings and air frames. The material is obtainable as sheet (ASTM B265), rod (ASTM B348, castings (ASTM B367), forgings (ASTM B381) and also as bolts and nuts (ASTM F467). The MIL number is T-9047.
In table 1 we see clearly how the effects on mechanical values depend on increasing degrees of impurity. We can also see the striking behaviour of alloy grade 5.

The engines alone of the Airbus A380 use about 11 tons of titanium.

Grade	Yield strength (in MPa)	tensile strength (in Mpa)	elongation (in %)
1	170-190	240-345	25-27
2	240-345	345-450	20-24
3	380-460	450-595	18-25
4	480-560	550-685	15-23
7	280-350	345-480	20-28
11	170-220	240-345	25-37
5	830-910	900-1000	10-18

Table: Mechanical values of some types of titanium.

The Vincent van Gogh Museum has a roof clad with titanium.

Seawater and atmospheric conditions

There are titanium products that guarantee continual use of titanium in seawater for 40 years without steps having to be taken to prevent corrosion. And when titanium is used in buildings as cladding for facades or for roofs a guarantee of as much as 100 years is given. Plenty of examples exist in Japan, and also the Guggenheim Museum in Bilbao and the Vincent van Gogh Museum in Amsterdam, which have respectively a facade cladding and a roof cladding.

Titanium as an alloying element

Titanium is used as an alloying element in for example stainless steel and also in sometimes in alloys of nickel, zirconium and vanadium. A well-known application is titanium used as a stabiliser in stainless steel grades with a high carbon content. For titanium has a high enough affinity with carbon for these two elements to form a compound at high temperatures. Thus it is possible to prevent harmful chromium carbides forming in for example heat-affected zone while welding. An example is 316Ti (1.4571), often used in Germany. However, this type of stainless steel is falling into disuse because nowadays it is also possible to prepare a low-carbon grade stainless steel in a commercially responsible fashion. This obviates the need for a titanium addition, since the risk of harmful chromium carbides forming has disappeared. This does not mean that titanium does not have a positive influence on the mechanical characteristics of austenitic stainless steels. For this reason a titanium-stabilised material is generally preferred to a low-carbon version for pressure vessels.

Shape memory alloys

Shape memory alloys (SMA), also called Nitinol, is an alloy of titanium and nickel (50/50). SMAs, after undergoing limited deformation at a relatively small rise in temperature, completely reverts to their original shape through the conversion of heat into mechanical energy.

Both processes have to do with a change of structure in the metal from austenite to martensite. This deformation of the shape memory metal occurs at room temperature and at warming of around 60°C. At this temperature the material has undergone a change in its structure. Supposing we have a straight piece of wire that we deform at room temperature, then it will revert to its original straight form at a temperature of around 60°C through the conversion of heat into mechanical energy. This mechanical energy can be used to activate something. The deformation must remain within a maximum of 8%, which means that the wire must never be bent. One can also use the so-called pseudo-elastic effect of this alloy, a well-known example being elastic spectacle frames.

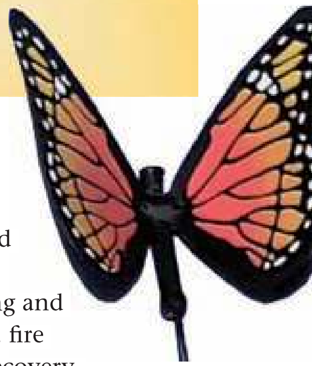
Much could be said about the production of SMAs, but it is not relevant enough to dwell on in detail. The summary presented below is designed to give an overview, though it should be stressed that the procedure is not a simple as it may sound: practice shows that the issues surrounding smelting, alloying and heat treatment require a great deal of expertise and experience. After the alloy has been smelted and brought into the required shape in a special vacuum, a pig is formed that is then drawn out to form a billet. It can then be rolled to form various products, which thereby attain their definitive form. These products are given a special heat treatment before leaving the factory.

To give a concrete example, let us suppose that a spring is to be made from SMA. We proceed as follows:

A rolled straight wire is wound and attached to a mandrel to a certain pitch. Depending on the wire thickness the whole thing is placed in a vacuum oven for some time at a temperature of around 500°C. After this heat treatment the wire will assume the form of the spring as its definitive form.

If the spring is picked apart at room temperature so that it takes on, say, an irregular form, the spring form will be completely restored at a temperature of around 60°C through the conversion of heat into mechanical energy. One can give the spring other forms by applying other heat treatments. However, the memory effect can to a certain extent be lost by overloading the mechanism or by exposing it too excessive temperatures.

Nitinol shape settings from Norman Noble, Inc.



Nitinol can be applied in process industries, above all in measuring and regulating technique, fire prevention, energy recovery, aerospace and even novelty articles. Because this titanium alloy is also bio-compatible it can be implanted in a human body. Examples are the fixation elements for broken bones, wires for scoliosis patients, stents to prevent blood clots during operations, prostate elements, elements used in operations on the spinal column, etc.

I would like to thank the Titanium Information Group (TIG) for giving me the information and inspiration necessary for writing this article. ■