

# A SURVEY OF GERMAN RESEARCH AND DEVELOPMENT WORK ON TITANIUM

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BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE

A SURVEY OF GERMAN RESEARCH AND DEVELOPMENT

WORK ON TITANIUM

Reported

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In view of the applications of titanium and the similar high melting point elements vanadium and chromium as possible base metals for high temperature materials, it was considered essential to obtain information from all available sources in Germany on the research and development work on these materials which had been done there. Prior to the war, little relevant information had been published, and the only indication of German interest in the subject came from Gottingen University, where Professor Vogel in collaboration with several other research workers, had published equilibrium diagrams in which titanium was one of the constituents. Some of these papers, such as that of Witte and Wallbaum on the iron-titanium system, gave tentative diagrams up to 100% titanium, which indicated that the authors might possess useful information on the technique of handling high titanium materials, these being extremely reactive and difficult to handle by normal methods. It was likely in any case that the Gottingen workers would be able to put us in touch with other establishments engaged on similar work. The search for information was therefore begun at Gottingen. Information on other targets was gradually collected, and eventually the whole field was covered. The following is a list of targets visited.

1. Göttingen University C21/648.
2. Freiburg University C21/1913.
3. Technische Hochschule, Hannover. C21/591.
4. Technische Hochschule, Aachen. C21/863.
5. Technische Hochschule, Berlin. C21/330.
6. Technische Hochschule, Darmstadt C21/322.
7. Technische Hochschule, Stuttgart (also K.-W. Institut  
C21/84. für Metallforschung) 21/2.
8. Kaiser-Wilhelm Institut für Eisenforschung, Düsseldorf. 21/3.
9. Kaiser-Wilhelm Institut für Eisenforschung Clausthal-Zellerfeld.
10. Bergakademie, Clausthal-Zellerfeld. C21/326 21/3
11. Verein Deutsche Eisenhüttenleute, Düsseldorf. 21/1(b).
12. Staatlicher Materialprüfungsanstalt, Berlin. 21/3(a).
13. Auer-Gesellschaft, Berlin. C21/371.
14. Siemens-Wernerwerke, Berlin. 21/22.
15. Osram, Berlin. C21/192.
16. Telefunken, Berlin. C21/1073.
17. Krupp, Essen. 21/11.
18. Goldschmidt, Essen. 21/31.
19. I.G. Farbenindustrie, Leverkusen. 21/34.
20. Gesellschaft für Electrometallurgie, Letmathe. C21/702.
21. Gesellschaft für Electrometallurgie, Nürnberg. C21/364.
22. Hereaus Vacuum Schmelze, Hanau. 21/21.
23. Metallbank und Metallurgische Gesellschaft, Frankfurt. C21/1914.
24. Metallwerke Plansee, Reutte. C21/124.

1. Metallographische Laboratorium, Göttingen University

Professor Vogel, Director of the Metallographische Laboratorium, stated that most of the work on binary alloy systems of which titanium was one constituent had been done by H.J. Wallbaum and H. Witte, the former being the metallurgist in charge of the work and the latter a physicist responsible for the X-ray work. Neither of these men was available for interrogation. It was ascertained that Wallbaum had become a member of the Waffen S.S. and is a prisoner of war. It is not known in whose hands. Witte was stated to have left Göttingen in 1939, and was thought to be at the Technische Hochschule, Darmstadt.

Under the direction of Professor Vogel, a large number of ternary systems including titanium and vanadium as one of the components had been investigated. The work had been carried out at the request of, and financed by, the Deutsche Forschungsgemeinschaft, in Vogel's opinion at the original instigation of some industrial establishment wishing to find a use for titanium metal. The Deutsche Forschungsgemeinschaft contributed R.M. 100,000 per annum and the state R.M. 12,000. This money was used to finance the Metallographische Laboratorium, which at the end of the war had a personnel of 12 as well as the professor.

The following systems had been investigated :-

1. Fe - Ni - Ti, the iron corner up to  $Ni_3Ti$  and  $Fe_2Ti$
2. Fe - Cr - Ti, in the region Fe -  $Fe_2Ti$  -  $Cr_2Ti_3$  - Cr
3. Fe - W - Ti, in the region Fe -  $Fe_2Ti$  -  $Fe_3W_2$
4. Fe - Si - Ti, in the region Fe -  $Fe_2Ti$  -  $FeSiTi$  - FeSi
5. Fe - C - Ni - Ti. This was done in an endeavour to replace nickel by titanium while obtaining steel of the same strength.
6. Fe - S - Ti, This was an attempt to remove sulphur from iron.
7. Fe - Si - V, in the region Fe - FeSi -  $VSi_2$  - V
8. Fe - S - V, in the region Fe - FeS - VS - V
9. Fe - Nb.

The methods used for the establishment of these diagrams were those of microscopical examination and thermal analysis. The metals were melted in a sintered corundum crucible in a Tamman furnace, which consists of a graphite crucible heated directly by a low voltage current. The temperatures were measured by means of a platinum/platinum-rhodium thermocouple. The highest temperatures reached were about 1600°C. X-ray methods were sometimes used to confirm observations. The apparatus used was extremely primitive, and the materials far from pure. The titanium was for the most part obtained in the form of ferro-titanium, although for the higher titanium alloys some van Arkel material from Eindhoven had been used. The melts were made under atmospheres of argon and hydrogen, for the purification of which no special precautions were taken. The resultant melts appeared to contain considerable amounts of foreign matter, such as pieces of the corundum crucible and thermocouple sheath. In view of these facts it is felt that no great reliance can be placed on the results of these investigations.

During the interrogation Professor Vogel mentioned work done on sintered mixtures of iron and iron sulphide, which he claimed could be made to give better strength properties than iron, owing to a precipitation hardening effect, and also the fact that the preparation of ductile silicon had been achieved in Germany, though he could not say where. The material was apparently required as a substitute for platinum. Vogel pointed out that he had only been concerned with the actual determination of the equilibrium diagrams, and had no knowledge of any use to which his results had been put.

Professor Masing, Director of the Institut für Metallkunde of Gottingen University, was also questioned, but added nothing to the information obtained on titanium.

Osram, Berlin.

Dr. Dawidl, the head of the hard metal and carbide department, was interrogated. - He said that Osram were interested in producing a high temperature material for use as a blade material for jet propulsion aircraft. Although for the most part their laboratories were concerned with hard metals and carbides they had been led to include titanium as a possible high temperature material, having previously produced the metal for gettering purposes. The firm was bound by agreement to communicate all results on carbides and cutting tool materials to Krupps at Essen, but since titanium was not included in this group, the work had been confined to Osram.

The firm first produced titanium metal by the reduction of titania with calcium hydride in an atmosphere of hydrogen at 800°C. The titanium hydride formed is then heated to 1100°C. and decomposes to titanium metal. The final product had a purity of only 90%, the chief impurities being oxygen and nitrogen. It was found possible to sinter this material, but after sintering it was naturally very brittle, and could only be rolled when hot. The rolling was done between iron sheets at a temperature of 800°C. The powder, the grain size of which was 10 - 20 microns, was used as a getter. It would have been better if the powder were finer, but no milling process was used. The reaction was carried out initially in nickel boats, but for efficient gettering the powder must contain less than 0.01% nickel, and the nickel boats were eventually replaced by molybdenum. Calcium oxide was removed from the powder by treatment with formic acid.

Alloys of titanium with nickel, cobalt, iron and copper had been prepared as part of a process for the preparation of artificial hard materials composed largely of titanium boride. The alloys contained 5 - 10% of these metals, the remainder being titanium. They were found to melt at about 1300°C.



The crucibles used were either titanium monoxide or densely sintered calcium oxide. Titanium monoxide is unsuitable for the melting of pure titanium, owing to its low melting point; but calcium oxide may be used if suitably sintered.

It was found possible to purify the titanium alloys by the addition of further quantities of calcium, the oxygen and nitrogen combining with the metal and being removed when the alloy was in the molten state. The purified alloys so produced were used in the preparation of titanium boride, and also for coating iron and steel sheet. This titanium-clad sheet was found to be extremely resistant to atmospheric and sea-water corrosion. The alloys were capable of being hot-rolled but could not be said to be ductile. Their micro-hardness was about 400 - 500 Kg./mm.<sup>2</sup> and it was considered that they might be useful for bearings working at elevated temperatures as the fritting temperature is unusually high, and there would thus be less likelihood of the bearing seizing up.

A translation of Dawihl's report on this work is included as an appendix.

Technische Hochschule, Hannover

The person of interest at this target was Professor W. Biltz, who was found to have died about a year previously. His successor, Professor Fischer of the Department of Inorganic Chemistry, said that the work of Biltz had been only on the sulphides and phosphides of titanium and not on the metal itself. Fischer himself had worked on the purification of titanium salts, and described a method by which the titanium is precipitated out from concentrated hydrochloric acid as titanium ammonium chloride. This salt is very insoluble in concentrated hydrochloric acid, and gives a good separation from impurities. Fischer said that he had considered the possibility of preparing pure titanium metal from the titanium ammonium chloride by Kroll's method of reducing the chloride with magnesium, but he had done no work on it. The purification process has been described in the Zeitschrift für anorganische und allgemeine Chemie in 1942 or 1943.

Interrogation of Professor Matting, Director of the Institut für Metallkunde, yielded no further relevant information.

Technische Hochschule, Stuttgart, and Kaiser-Wilhelm  
Institut für Metallforschung, Stuttgart.

These two research establishments were occupying the same premises, and appeared to be sharing personnel.

Dr. Kubaschewski, who was acting as head of the metallurgical department in the absence of Dr. Grube in prison, introduced Dr. Speidl, said to be engaged on titanium research.

On interrogation, Dr. Speidl said that he had been commissioned to work on titanium by Hereaus Vacuum Schmelze, Hanau. He had planned a complete study of the properties of the material beginning with the preparation of the pure metal, which he intended to do by the van Arkel process. He had been just about to begin the experimental work when the end of the war put a stop to all such research. He could not say why Hereaus had commissioned the work.

Hereaus Vacuum Schmelze, Hanau.

In view of the information obtained from Dr. Speidl, Stuttgart, Dr. Ruthardt of the firm Hereaus at Hanau was interrogated. He said that the firm's interest in titanium was due to the Onsmettingen branch, who considered that it might have very useful applications in the production of mirrors owing to its excellent resistance to corrosion and condensation. The process involved the evaporation of a very thin layer of titanium on to a glass surface, starting with the ductile material. They were therefore interested in the production and properties of ductile titanium and had commissioned Dr. Speidl to work on it. Dr. Ruthardt was not aware that similar work was being done by Osram in Berlin.

THE PRODUCTION OF TITANIUM METAL

by

Dr. W. Dawidl

The reduction of titanium dioxide with calcium hydride was first carried out in order to investigate the properties of titanium metal as a constructional material and also to produce and investigate such compounds as titanium boride. The calcium hydride was obtained from I.G. Farbenindustrie at Bitterfeld. The reduction of titanium dioxide with calcium hydride is self-sustaining after ignition. Calcium hydride is very sensitive to attack by water, and the grinding and mixing of this material with titanium dioxide must be carried out rapidly and as far as possible in the absence of air. The titanium dioxide was obtained from I.G. Farben at Leverkusen, and had to be fired to about 500°C. before use to remove all traces of water.

The reduction itself was carried out in a continuous-feed furnace consisting of an iron tube 5 metres long and 6 cm. diameter, heated electrically to 600 - 700°C. The tube was kept full of pure hydrogen which had been dried over silica gel and phosphorus pentoxide. Any traces of oxygen in the hydrogen were previously removed by passing it over heated copper.

In order to prevent an excess of gas from passing over the charge, hydrogen was only admitted while a boat was being placed in or removed from the furnace. During the reaction time a low pressure of hydrogen was maintained in the furnace. When the furnace was opened the hydrogen was led away through a duct and not allowed to ignite, in case this led to condensation of water inside the furnace tube, or more particularly

inside the coolers.

In this way the reaction was carried out without any disadvantage excepting the discontinuity involved in using iron pots.

For the reaction, 1 kg. of freshly fired titanium dioxide was mixed with 1.3 kg. of calcium hydride. The calcium hydride was ground by hand and then mixed with the titanium dioxide, previously dried for 24 hours, in a porcelain ball-mill. The mixture was then pressed into boats 3 cm. long and 5 cm. outside diameter. The boats were originally made of nickel. The use of the titanium metal so produced in the valve industry showed that small but harmful amounts of nickel had been picked up, and hence molybdenum boats were subsequently used instead of nickel. Each boat held a charge of 350 gm. and gave a yield of 70 gm. of titanium metal.

After introduction into the furnace, the charged boat is pushed into the reaction zone by means of an iron bar. The bar passes through a gas-tight gland. After the reaction is completed the boat is pushed into the cool zone and a new boat introduced. It must be noted that it is necessary that the transformed mixture should be cooled as rapidly in order to minimise the harmful effects of the gas atmosphere. The reacted charge should appear a uniformly grey colour throughout, and should contain no black grains.

The contents of the boats were emptied into sealed bottles. The next treatment was crushing in a mortar, followed by pickling in a 30% solution of formic acid. The formic acid was 50% in excess of that required theoretically. After the first treatment the liquid was decanted off and a second pickling in the same quantity of acid carried out. The remaining material was washed with distilled water to which had been added a small quantity of formic acid, followed by a simple washing operation

and drying in vacuo. The residual material (approximately  $TiH_2$ ) was converted into titanium metal by heating in vacuo to  $1100^{\circ}C.$ , when the hydrogen came off, leaving 94 - 97% titanium.

### Applications of Titanium Metal

#### 1. For getter material.

The firm Telefunken used titanium as a substitute for other getters such as zirconium with complete success. The titanium was applied either by dipping or by cataphoresis.

#### 2. Titanium alloys.

Telefunken have also tried out titanium alloys as a substitute material for rectifier plates and cathodes in place of the nickel-aluminium alloys previously used. The investigation was not completed at the end of the war, but indications had been received that a nickel-titanium alloy had good possibilities.

#### 3. As a corrosion-resistant and hard-wearing material.

Experiments on the corrosion resistance of sintered pure titanium and of alloys of titanium with cobalt, nickel and iron showed that polished test-pieces, after being allowed to stand in damp air, after dipping in sea-water, and after spot tests with sea-water, had maintained their high polish after a four-week period.

The micro-hardness of pure titanium sintered for one hour at  $1100^{\circ}C.$  in vacuo gave results in comparison with other materials as follows :-

Sintered titanium metal	475 kg./mm. <sup>2</sup>
Sintered pure iron	100 - 150 kg./mm. <sup>2</sup>
Sintered steel with 0.4% carbon	350 kg./mm. <sup>2</sup>
High speed steel (hardened)	850 kg./mm. <sup>2</sup>
Primary tungsten carbide in melted hard metals	3000 kg./mm. <sup>2</sup>

The determination of adhering temperature as a measure of the speed in cutting for dry friction gave :-

Sintered titanium metal against steel of 40 kg./mm.<sup>2</sup> strength 800°C.

Sintered titanium metal against steel of 120 kg./mm.<sup>2</sup> strength 925°C.

Steel with high speed steel 600°C.

A determination of the tensile strength of pure sintered titanium metal gave a value lying between 10 and 30 kg./mm.<sup>2</sup>. The highest observed extension was 4%.

In spite of the relatively low strength of titanium, it has the advantage over iron that it has a higher micro-hardness and a higher adhering temperature, so that it should have a greater cutting speed when used dry.

Tests which have been carried out on a bearing testing machine showed that sintered titanium has very good life properties.

The relatively low extension and the impossibility of cold working the titanium metal shows that there is too high

a percentage of dissolved oxygen in the metal to obtain a truly ductile sample of titanium. By hot rolling at 900°C. the sintered titanium could be formed into sheets. The rolled sheet, however, showed considerable tearing at the edges and cracking across the surface. A metallographic investigation indicated that no appreciable deformation of the crystals had occurred, but quite definite slip planes could be discerned. Hence the deformation must have occurred by gliding of the grain boundaries.

Titanium metal appears to favour the formation of rounded crystals, as do the carbides of titanium vanadium and molybdenum. As the investigation on rounded crystal formation in these carbides has shown, these are extremely unfavourable for good mechanical properties. (See Handbuch der Hartmetalle). Thus the discovery of the cause of rounded crystal formation is not only fundamentally important for the improvement of the above carbides but also for titanium and its alloys.

In spite of the small elongation, we have hot rolled titanium sheet as well as sheets of alloys of titanium with 5% cobalt, 5% iron and 5% nickel, and alloys with copper and silver containing additions of high melting point metals such as chromium. We have also rolled together titanium and iron sheet. These materials were easily polished, and as previous laboratory tests had shown, they gave an extremely good corrosion resistance to the iron so treated. Up to 400°C. such sheets as were rolled on to iron proved to have no cohesion with 100 kg./mm.<sup>2</sup> steel. The apparatus used did not permit higher temperatures to be investigated.

Furthermore, we have carried out experiments on the melting of titanium and its alloys using titanium monoxide and calcium oxide crucibles. The calcium oxide crucibles were produced by sintering at a temperature of 2200°C. The finished product was translucent, and was able to withstand



many days immersion in water. The titanium monoxide  $TiO$  was produced by the reaction of titanium metal with titanium dioxide, and was sintered at  $1700^{\circ}C$ .

Titanium alloys could be melted in iron, and gave good adhesion strength.

To conclude, there are a number of possible uses for a 96% titanium metal which may be able to be developed, namely:-

1. As titanium powder for getters.
2. As a corrosion resistant material either alone or alloyed to other metals in the form of sheets which can be rolled on to the material to be protected, or melted on to it.
3. As a cutting material, especially for dry cutting.
4. The alloys may be usable if the elongation can be increased.

#### Experiments on the improvement of the ductility of titanium metal and its alloys

In order to improve the ductility we have carried out a large number of laboratory experiments. The investigations have in many cases given a considerable improvement in the ductility and especially in the elongation during tensile test. Up to the present we have not been able to obtain good reproducibility in the results due to our inability to control all the conditions affecting the product, so that we cannot claim that a particular method will give ductile titanium in every case. Consequently we will only give a review of the methods we have used. Since we have not examined a range of conditions we cannot give an exact description of the processes.

#### 1. Alloy Research

The initial material was 95% titanium obtained by reduction with calcium hydride. Since it is impossible to

remove completely the last traces of oxygen in titanium by additions of magnesium or calcium, we thought that a disturbance of the titanium lattice by addition elements may produce an easier method of deoxidising the molten metal. To this end we have heated titanium metal powder with calcium and magnesium metal (up to 90% additions) to the melting point of calcium or magnesium, and have then made additions of cobalt, nickel and iron to the alloys. These alloys proved to be able to be cold rolled, and showed metallographically that the crystals themselves had been deformed. Glide planes could often be observed. Treatment of the calcium and magnesium alloys with formic acid and very dilute hydrochloric acid increased the purity up to a maximum of 99% titanium. The average figure obtained was 98% titanium, the remainder being largely calcium or magnesium. Sintered rods of this type of titanium metal showed elongations up to 3% and tensile strengths considerably higher than those of the original high-oxygen-containing powder.

## 2. Melting Experiments

In order to determine how much oxygen is driven off by melting titanium, we have melted the titanium powder in the form of sintered bars in calcium oxide crucibles. It was necessary to maintain the temperatures very close to the melting point in order to prevent reaction with the crucible material. We have had greater success in melting the titanium using a tungsten arc. It was very difficult to melt large quantities of titanium with sufficient uniformity in this arc. We therefore arranged the titanium bar so that it hung vertically downwards, and an arc was struck with a large tungsten electrode. Around the tungsten electrode were two cylindrical molybdenum sheets concentric with the electrode. The space between the sheets was filled with tungsten wool, the whole serving as a radiation shield. The whole apparatus was sealed into a hard glass vessel, and made vacuum tight. The titanium metal which

dropped down was caught in a calcium oxide crucible placed directly below the melting titanium. The crucible was heated by molybdenum wire in order to form the dropping titanium into a coherent body. In this way the melting can be carried out either in vacuo or in a protective gas atmosphere. For vacuum melting we have used a quartz vessel which can be heated to higher temperatures, hence making a more convenient form of apparatus.

Before beginning the melt, the calcium oxide crucible was filled with molten calcium in order to remove the last traces of moisture. A liquid air trap was also included in the apparatus to collect any water vapour.

Titanium metal produced in this way was found to be 98 to 99% pure.

During the melting experiments, one melt was made in a hydrogen atmosphere under pressure in order to try to obtain a greater reduction of the oxygen in the molten titanium. In our apparatus only a few atmospheres excess pressure could be used. Thus we found no effect due to the excess hydrogen pressure. It is to be expected that higher pressures may give a useful amount of reduction.

### 3. Vaporisation Experiments

Experiments on the vaporisation of titanium which had been reduced with calcium hydride in a high vacuum produced little or no separation from oxygen. It does not seem possible, therefore, to purify the metal in this way.

### 4. Dissociation of Halides on a Heated Wire

As a result of the research carried out by van Arkel and de Boer, together with workers in the Osram Research Laboratories, titanium can be prepared in a very pure form free from oxygen by the decomposition of a titanium halide on a hot tungsten filament.

The development of this method was only completed shortly before the end of the war. Because of the difficulties involved in the use of the tetraiodide, we used the tetrabromide. The tetrabromide was prepared by passing bromine over titanium carbide, which was easily and cheaply obtained. In the apparatus under construction a large number of parallel wires were suspended. It was calculated to produce 1 - 2 Kg. of titanium in 24 hours. The apparatus is no longer available. (A diagram of the proposed arrangement is given at the end of the report).

#### 5. Behaviour of Titanium Alloys

Alloys of purified titanium with iron, nickel, cobalt and copper show melting points of about  $1300^{\circ}\text{C}$ . for 90% or more of titanium. These alloys can be hot rolled at 800 to  $900^{\circ}\text{C}$ . to sheets of good quality, and can also be rolled on to iron plates.

Alloys of grey cast iron with titanium gave extraordinarily high hardness values, the actual figures for which have not yet been determined.

The alloying of other metals with titanium was carried out during the reduction of titanium oxide with calcium hydride. It was shown that by so alloying, a considerable reduction in oxygen content was produced. Analysis figures are not now available.

