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METHOD OF MAKING TITANIUM ALLOYS

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The invention relates to a method of making alloys of titanium. It more particularly concerns an improved method of making alloys of titanium in which the alloying is accomplished during the reduction of titanium tetrachloride with magnesium in making titanium sponge.

The principal object of the invention to obtain uniformity of distribution of alloying elements throughout the titanium alloy. Other objects and advantages will appear as the description of the invention proceeds.

The term "alloying element" as used herein and in the appended claims means any solid element or group of solid elements capable of forming an alloy with titanium, e. g. Ag, Al, Au, B, Be, Bi, C, Cb, Ce, Co, Cr, Cu, Fe, Ga, Ge, Hf, In, Ir, Mn, Mo, Ni, Os, Pb, Pd, Pt, Rh Sb Si, Sn, Ta, Tl, Th, U, V, W, Zr.

In our copending application Serial No. 315,604, filed October 20, 1952, we have disclosed and claimed a method of reducing titanium tetrachloride vapor with magnesium to form a sponge of titanium. According to the method so-disclosed, the magnesium is used in the form of particles which are deposited as a pile upon a supporting surface, such as a steel plate, the temperature of which is subject to control. The titanium tetrachloride vapor to be reduced forms the atmosphere around the particles which are permitted to burn in the titanium tetrachloride vapor at only a smoldering pace that is without producing a noticeable flame by abstracting a sufficient amount of the heat of the reducing reaction through the supporting surface to keep the burning of the particles at a smoldering pace. As the magnesium particles thus smolder titanium sponge forms along with molten magnesium chloride as a by-product which partly drains out of the sponge. After the smoldering ceases, the resulting titanium sponge, which still contains some magnesium chloride, is removed from the supporting surface as by scraping. The magnesium chloride in the sponge is removed in any suitable manner as by sublimation, leaving chloride-free titanium sponge as the end product.

We have now discovered that by including a solid alloying element in particulated form with the particulated magnesium, which is subjected to a controlled smoldering in titanium tetrachloride vapor as in the foregoing method, an unmelted solid titanium sponge is obtained in which the alloying element is uniformly distributed throughout the sponge. Subsequent melting of the sponge yields a uniformly alloyed titanium. The invention then consists of the improved alloying method herein fully described and particularly pointed out in the claims.

In carrying out the invention, the particle size of the element to be alloyed with the titanium does not appear to be sharply critical, although better alloying results are had with small particles, such as those passing through a No. 50 standard sieve with 90 percent retention on a No. 325 sieve. Particles smaller than those passing through a No. 325 sieve are not desirable. The particle size of the magnesium used is preferably made

about the same as that of the alloying element. The particulated alloying element and the particulated magnesium are mixed together so as to form a uniform mixture of the alloying element and the magnesium. The relative amounts of the alloying element and magnesium used depends upon the proportion of alloying element it is desired to produce in the titanium alloy to be made. The proportions may be determined by due consideration of the stoichiometrical relations involved in the reaction which ensues when the mixture of magnesium and alloying element is subjected to smoldering in an atmosphere of titanium tetrachloride in accordance with the invention. In the smoldering reaction, the magnesium reacts with the titanium tetrachloride without substantial attack on the aloying element according to the following equation:

$$2\,Mg+TiCl_4=Ti+2\,MgCl_2$$

From this equation, it is manifest that on completion of the reaction 48.64 pounds of magnesium theoretically yield 47.9 pounds of titanium, or to produce 99 pounds of titanium theoretically requires

$$\frac{99\times 48.64}{47.9}=101.6 \text{ pounds of magnesium}$$

Hence, to produce 100 pounds of titanium alloy containing 1 percent of alloying element requires 101.6 pounds of magnesium mixed with 1 pound of alloying element. In other word, the mixture of magnesium and alloying element to produce a titanium alloy containing 1 percent alloying element requires a magnesium-alloying element mixture containing

$$\frac{1}{102.6}\times 100=0.985 \text{ percent}$$

of alloying element in the mixture of particulated alloying element and particulated magnesium. Other proportions may be calculated in similar manner.

The mixture of particulated magnesium and particulated alloying element, in the proportions necessary for the production of the desired titanium alloy composition, is deposited upon a temperature-controlled supporting surface in an atmosphere of titanium tetrachloride vapor in a reaction zone where the reduction of the vapor is to take place. The supporting surface is suitably heated to a temperature sufficient to initiate smoldering of the magnesium in the mixture, a temperature of about 500° to 950° C. being sufficient. After smoldering begins, heat is removed from the smoldering pile, as by cooling the supporting surface, at a rate sufficient to prevent the pile from bursting into flame while maintaining combustion at a smoldering pace until the magnesium is consumed. As the magnesium smolders, metallic titanium forms in situ as a solid sponge with the particles of alloying element, originally mixed with the particulated magnesium, uniformly distributed in the sponge together with magnesium chloride as a by-product. It is preferable to maintain the supporting surface at least hot enough to melt the by-product magnesium chloride (M. P. 708° C.) so that much of it will drain off the sponge while forming. After the sponge containing the alloying metal has formed, it may be dislodged from the supporting surface by means of a cooled scraper and removed from the titanium tetrachloride vapor reaction zone. The residual magnesium chloride remaining in the sponge after draining and the removal from the titanium tetrachloride vapor reaction zone may be removed in any suitable manner. A preferred method of removing the residual magnesium chloride is to subject the crude sponge to sublimation by heating it in an inert atmosphere to a temperature sufficient to vaporize off the magnesium chloride. The resulting chloride-free titanium

sponge containing the alloying element may be worked into massive uniformly alloyed titanium metal by melting, as by means of an electric arc in an inert atmosphere, and solidifying the melted sponge.

The following example is illustrative of the practice of the invention:

Example

150 pounds of atomized magnesium and 4.5 pounds of atomized aluminum, passing through a No. 20 standard sieve but not through a No. 200 standard sieve, and 7.5 pounds of electrolytic chromium powder, passing through a No. 200 standard sieve but not through a No. 325 standard sieve, were mixed together to form 162 pounds of a uniform mixture of the three particulated metals. The mixture was fed onto a moving hearth maintained at a temperature of 750° C., the rate of feed and travel of the hearth resulting in the formation of a train of the metal particles on the hearth about ½ inch deep, 1½ inches wide at the rate of 1 lineal foot per minute. An atmosphere of titanium tetrachloride vapor was maintained around the train at a pressure of about 4 inches of water above atmospheric pressure. The train smoldered on the hearth as the train formed and reached reaction temperature and increased in bulk as the magnesisum in it was consumed forming titanium sponge at the rate of about 1 lineal foot of sponge per minute, and molten magnesium chloride. The molten magnesium chloride partly drained out of the sponge as it formed. After the magnesium was consumed, as indicated by the cessation of smoldering, the resulting sponge was scraped off the hearth, removed from the titanium tetrachloride vapor, and collected.

During the collection of the sponge, 17 samples were

taken at approximately equal intervals of time and analyzed for Al and Cr. The average of the analysis showed an Al content of 2.9 percent and a Cr content of 5.2 percent and the maximum deviation of the individual analysis from the average did not exceed ±0.14 per cent. Six samples of the sponge were arc melted together in a water cooled copper mold in an inert gas atmosphere forming a titanium alloy ingot of uniform composition having a density of 0.163 pounds per cubic inch.

We claim:

1. The method of making an alloy of titanium and a solid element alloyable therewith which comprises forming a mixture of magnesium in particulate form with the alloying element in the particulate form, supporting the mixture on a surface in an atmosphere of titanium tetrachloride vapor, and maintaining the surface of support at a temperature permitting the magnesium to burn only at a smoldering pace whereby titanium sponge is formed having uniformly dispersed therethrough the alloying element, and removing the so-obtained titanium sponge from the surface of support and the titanium tetrachloride atmosphere.

2. The method according to claim 1 followed by melting the titanium sponge and solidifying the melted sponge.

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