RECYCLING OF TITANIUM CHIPS
J. Bergreen, Messerschmitt-Bölkow-Blohm GmbH, Augsburg, FRG

Introduction

The raw material required for the production of titanium and titanium alloys is titanium sponge. Titanium sponge is produced commercially by chlorinating rutile or ilmenite and reducing the titanium tetrachloride thereby obtained using magnesium or sodium as the reducing agent. The processes involved have a high energy requirement and as a result the price of titanium sponge is relatively high. Fig. 1 shows the trend in titanium sponge prices from 1966 to 1984.

![Graph showing the trend in titanium sponge price from 1966 to 1984](image)

Fig. 1: Trend in titanium sponge price in the period 1966-1984

It can be seen that two factors have had a major bearing on this price trend. There was a sharp rise at the beginning of the energy crisis in 1973/74 and a further drastic increase in the late 70s as a consequence of the shortage of titanium sponge worldwide. After the near doubling of titanium sponge manufacturing capacity and also as a result of the recession in the aircraft industry, the price has again stabilized at a lower level.

Titanium raw materials costs are high in comparison with other engineering materials, and recycling has been undertaken ever since titanium was first produced commercially. Titanium producers reprocessed their in-plant scrap produced
during the manufacture of semis and recycled it directly to the melting process. This was mainly bulk or small-size scrap whose reprocessing does not present any major problems. Scrap statistics show that in the past the USA has recycled titanium particularly intensively. In 1980 the titanium scrap share in the melting process was about 37%. For Europe the figure is estimated to be 15 to 30%.

The macroeconomic benefit of titanium recycling is twofold: energy consumption is markedly reduced and raw material stocks are made to last longer. Fig. 2 clearly shows the energy saving that can be made by recycling titanium.

![Energy Saving Graph](image)

**Fig. 2: Effect of the percentage of scrap on total energy consumed in producing titanium (5)**

If 50% scrap is incorporated in the consumable electrode which is melted down to produce titanium, the total energy requirement drops by 45%. If the share of recycled material is further increased, energy consumption is reduced to 10% of what it would be if titanium sponge were used instead.

Since the amount of metal removed in the machining of titanium components for the aircraft industry is in some cases as high as 90%, significant amounts of titanium chips are produced. In the past these chips were mostly sold to the steel industry for alloying purposes. Investigations were started a long time ago, however, into possible ways of reprocessing these chips in the titanium industry (1-18). The aim of the experiments was to develop a titanium reprocessing technique which removed all harmful impurities, cemented carbide particles in particular, and which could be applied on a large scale. The work was performed in close collaboration between Schmiedewerke Krupp-Klöckner GmbH, Essen, and Messerschmitt-Bölkow-Blohm GmbH (MBB), Augsburg in the period 1977-1981. To make commercial-scale application possible, the point of scrap production had first to be sealed off and quality assurance measures applied at the Augsburg...
works. J. Berggreen will be reporting on this in his paper entitled "Requirements for the recycling of valuable chips from and for Aircraft Manufacturing".

Outline of the reprocessing method

The milling chips of the titanium alloy Ti Al6 V4 supplied by MBB in sealed containers are reprocessed in the steps listed in Table 1.

<table>
<thead>
<tr>
<th>No.</th>
<th>Process steps</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Air classification</td>
<td>Rough sorting of foreign bodies such as clamping elements, cemented carbide indexable inserts, screws, nuts etc.</td>
</tr>
<tr>
<td>2</td>
<td>Crushing</td>
<td>2 crushers in tandem with 8 and 5 mm screens</td>
</tr>
<tr>
<td>3</td>
<td>Centrifugation</td>
<td>Separation of excess cutting fluid</td>
</tr>
<tr>
<td>4</td>
<td>Washing and drying</td>
<td>Degreasing with perchloroethylene</td>
</tr>
<tr>
<td>5</td>
<td>Magnetic separation</td>
<td>High-intensity-field magnetic separator</td>
</tr>
<tr>
<td>6</td>
<td>Visual inspection</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>X-ray inspection</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Splitting</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Chemical analysis</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Packing and storage</td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Process steps in the reprocessing of titanium chips

The first step is air classification, which is carried out to separate lumpy impurities straight away. The possibility cannot be ruled out of carbide tools spalling during machining and the particles adhering to the titanium chips. If the weight ratio between titanium chip and carbide particle is too high the magnetic separator is unable to remove the carbide particles. The maximum chip size for crushing was therefore limited to 5 mm. On delivery, the swarf contains approx. 10 to 20% cutting fluid, which is largely removed by centrifuging prior to washing. In the washing unit, the chips are degreased and dried. Two washes may be necessary to reduce the slightly increased carbon content to < 0.1%. The titanium chips and magnetic impurities are separated by a magnetic separator operating with a high-intensity field. After magnetic separation, the chips are inspected visually.
to sort out non-magnetic impurities such as non-magnetic metals or titanium chips tarnished by oxidation.

X-ray inspection takes place in a continuous unit. The chips are carried past the X-ray tube on a 70-mm wide belt conveyor. The unit is adjusted so that spherical carbide particles \( \geq 1 \) mm in diameter are reliably separated. For this purpose a special blow-out mechanism is provided which is activated if carbide or high-density particles are present. In addition, a stationary check is made on the titanium chips for carbide impurities with a particle size of \( \geq 0.5 \) mm. The unit is calibrated prior to each inspection with spherical carbide particles \( 1 \) mm in dia. In the splitter downstream, the composition of the chips is homogenized, and at the same time samples are taken for chemical analysis. Before a batch of chips is released, the following elements are checked: \( \text{O, C, N, Fe, Al, Cu, Mn, Mo, Ni, Sn, V, W, Y, Zn, Zr} \). The average oxygen content of the milling chips is 0.23 %. The oxygen enrichment is due to the greater surface area of the chips compared with the compact material. Since current specifications lay down that the oxygen content of materials used in aircraft components may not exceed 0.20 %, the excess is offset by charging titanium sponge with oxygen contents of between 0.05 and 0.1 %.

**Remelting the chips**

In considering ways of remelting the chips it was assumed that only a consumable-electrode vacuum arc furnace would be available and that the chips would thus have to be incorporated in the electrode accordingly. This is done by compacting a blend of chips, titanium sponge and master alloys. To form stable compacts, a pressure of 600 N/mm\(^2\) has to be exerted. The maximum amount of chips that can be used is dictated by the stability required in the compacts. Actual operating practice has shown that if the consumable electrode to be used in the vacuum arc furnace contains up to 60 % chips, it still displays adequate stability.

**Considerations on dissolving high-density particles**

When deliberating the recycling concept it was purposely assumed that spherical carbide particles with a diameter of \( < 1.0 \) mm would still be present in the titanium chips after reprocessing. It has, therefore, to be ensured that these particles dissolve in the course of two remelting operations. Simulation tests were carried out to determine the melt-down of cemented carbide in titanium alloy melts and commercial-scale tests performed. The difficulty is that the findings from small-scale tests carried out to determine the rate at which cemented carbide dissolves in titanium melts cannot be applied to full-scale operation. For this reason, melting tests were carried out on 4.5-t ingots containing 2-mm dia. carbide particles. After double melting, the ingots were rolled to 30 mm plates and subjected to complete
X-ray inspection. It was verified that there were no longer any carbide inclusions present. The smallest detectable size of a carbide particle was 0.4 mm. It can thus be concluded that carbide particles ≤ 1.6 mm in diameter definitely liquify when the chips are remelted twice in a vacuum arc furnace. This has been confirmed in all subsequent melts.

Test results

Up to mid-1984 62 ingots of the alloy Ti Al6 V4, each containing up to 50% chips, were melted. This represents a total amount of approx. 310 t. A statistical evaluation of 81-mm thick plates produced the values listed in Table 2.

<table>
<thead>
<tr>
<th>Properties</th>
<th>MBB Specification</th>
<th>Sample direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rp0.2 N/mm²</td>
<td>830</td>
<td>L 937</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LT 979</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ST 928</td>
</tr>
<tr>
<td>Rm N/mm²</td>
<td>900</td>
<td>L 975</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LT 1010</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ST 976</td>
</tr>
<tr>
<td>A %</td>
<td>(8(6.5 ST)</td>
<td>L 15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LT 13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ST 12</td>
</tr>
<tr>
<td>Z %</td>
<td>20(15 ST)</td>
<td>L 33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LT 31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ST 28</td>
</tr>
</tbody>
</table>

Table 2: Mechanical properties of plates made of the titanium alloy Ti Al6 V4 with the addition of 50% chips.

The specified values are achieved with the reliability necessary in production. The values obtained are in good agreement with those derived from melts into which no chips were charged. As part of the procedure for obtaining the aircraft industry's approval for the recycling process, single-stage fatigue tests were carried out on 33- and 65-mm plates. The fatigue strength values determined at \( \alpha_p = 1.0 \) and \( R = 0.1 \) are around the 550 N/mm² mark. This is also the value obtained in comparative tests carried out on samples taken from material made without the addition of chips.

To verify the homogeneity of the macro- and microstructures, numerous metallographic sections were examined. No impurities or inadmissible inclusions whatsoever were found. The microstructure meets the standard prescribed by the Technical Committee of European Titanium Producers (ETTC 4).

The ultrasonic inspections carried out under the approval procedure were performed on all the plates rolled from a single heat. 82-mm rough-rolled slabs as well as 17, 28 and 33 mm finish-rolled plates were inspected. The prescribed standard was the American test specification MIL-I-8950 B, class AA, representing an equivalent flaw size of 1.2 mm.
Ultrasonic testing revealed no flaws whatever on any of the plates. Parallel to ultrasonic inspection, X-ray tests were also carried out in order to verify that no high-density particles, particularly carbide particles left from machining, were present. In all, 126 test areas were examined, two X-ray photographs being taken of each one. Webs to DIN 54109 and spherical carbide particles of between 0.4 and 1.0 mm in dia. were used for calibration. Assessment of all X-ray photos showed that no high-density particles of the stated size were present.

Discussion and outlook

Owing to the high degree of machining involved in manufacturing titanium alloy components for the aircraft industry, the proportion of titanium chips is relatively large in comparison with bulk and small-size scrap (2, 3, 4). As the cost of raw materials for titanium alloys rose, titanium manufacturers became increasingly interested in recycling titanium chips to the melting process. In the literature two main recycling processes are to be found. In the first of these, the titanium chips are cleaned and subsequently melted down in an electron-beam furnace or a non consumable electrode arc furnace, with the remaining carbide particles being separated in a tilting crucible or forehearth (2, 11, 13, 16). This process is mainly used for commercially pure titanium chips. Greater importance attaches to the second process, in which remaining carbide particles are separated by a high-intensity-field magnetic separator (1, 6, 7, 9, 10, 12, 13, 14, 17, 18). By way of subsequent testing (X-ray inspection, magnetic testing) it is additionally ensured that any carbide particles not separated by the magnetic-separator are removed. The latter two decisive steps, magnetic separation of carbide remnants and verification by X-ray inspection, are included in the reprocessing method described here. The tests have shown that on a commercial scale this process operates with the requisite reliability in production and that the addition of at most 50 % titanium chips does not cause any change in the properties of the titanium alloy Ti Al6 V4.

The use of chips in the production of titanium alloys for fabricating aircraft components was hitherto only regulated by the AMS specification 2380, August 1972, premium grade, which prescribed a 100 % X-ray inspection. In the revised specification brought out in 1983 the testing procedure is no longer specified but has to be agreed by the titanium manufacturer and the customer. The same wording is to be found in the tentative DIN standard 65437 and ETTC 6. These specifications take into account the application of new magnetic testing procedures which are capable of reducing the size of detectable carbide particles. The disadvantage of the magnetic method, however, is that non-magnetic particles of high density cannot be detected.
Here again, it is incumbent upon the quality assurance department to seal off the point where the chips are produced to ensure that prior to chip recycling, and during the recycling process itself, no high-density particles can find their way into the titanium swarf.

In the literature (15), the proportion of recycled material used in the production of titanium alloys is estimated to have increased from 10-15 to 35-40%. This increase is due in large measure to the advent of titanium chip recycling.

The cost-efficiency of titanium chip recycling depends on a number of factors. These include the price of titanium sponge, the cost of collecting the swarf and reprocessing expense. Account must also be taken of quality assurance and other requirements which have to be met to secure the aircraft industry's approval of the entire recycling process. Recycling is thus only appropriate if - as described in this report - titanium chips of a certain quality are produced in large amounts at a single place and are reprocessed by an approved method.

References
(9) Metal Bulletin (July 13, 1982) 17.
(10) K.-H. Kramer: 
(12) M.A. Vednjev, V.I. Drozzina, P.F. Michajlov, S.V. Ponedilko, S.M. Usov: 
(14) Technical Update No. 10 (April 26, 1984) 
Suisman Titanium Corporation, Hartford, USA.
(16) Deutsche Offenlegungsschrift DE 27 50 606 (24.5.78) 
Viking Metallurgical Corp., Verdi, Nev., USA.
Suisman + Blumenthal Inc., Hartford, Conn., USA.
(18) Deutsche Offenlegungsschrift DE 31 46 049 A1 (5.8.82) 
Suisman + Blumenthal Inc., Hartford, Conn., USA.