Research and Development of Low-cost Titanium Alloys

Xin Shewei, Zhang Jingli, Mao Xiaonan, Zhao Yongqing, Hong Quan
Northwest Institute for Nonferrous Metal Research, Xi’an Shaanxi 710016, China

Abstract. Excellent mechanical properties combined with low density, good corrosion resistance and welding, make titanium alloy attractive structural materials for aerospace, ship navigation, weaponry and nuclear industry. However, the high cost impedes the further use of titanium alloy in different fields, and which is the key factor for productivity and further use of titanium alloy. Aiming at lost cost of titanium alloy, three parts of raw material, alloy design and working forming were overviewed, which will offer reference for how to low cost of titanium alloy.

1. Introduction
Excellent mechanical properties combined with low density, good corrosion resistance and welding, make titanium alloy attractive structural materials for aerospace, ship navigation, weaponry and nuclear industry. Innovation and development of titanium alloy technology have been promoted in military industry. In particular, the development of this technology has been accelerated in aviation industry. Due to the high technology application, the cost of titanium alloy increases and keeps a high level. Thus, the use of titanium alloys has been limited in weapons, construction, automobile, sports and other fields. At present, the high manufacturing cost is the main problem limiting the application of titanium alloys, which prevents titanium alloys from being used as widely as steel and aluminum alloys. Once costs of titanium alloys are reduced, some materials in use in many fields can be replaced by titanium alloys [1,2] and the use of titanium alloys will increase exponentially. Therefore, the study on of low-cost titanium alloys and the low-cost production technology of titanium alloys become research hotspots in recent years.

In general, low-cost technology of titanium alloy can be implemented from raw material, alloy design and processing and forming. In this paper, the research and development of low-cost titanium alloys are overviewed in terms of the above three aspects.

2. Raw material
The content of titanium in the earth’s crust is about 0.6%, which is the fourth-most-abundant metal element lower than Al, Fe and Mg and the ninth-most-abundant element among all elements. Titanium is dispersed in nature and difficult to be extracted. Thus, titanium is considered as a minor metal element, which is not classified by the content. By way of example that nobody can drink from closed bottles, German electrochemical expert Prof. Fritz Scholz [3] explained that it is so difficult to completely reduce solid TiO2 to solid Ti. Therefore, the cost of raw material of pure titanium are determined by extraction and smelting process.

At present, the Kroll process formed in the late 1940s is still the most common method used in industrial production in the world, by which titanium sponge is produced by magnesiothermic reduction process. During the discontinuous process of production, operations such as charging, high-temperature heating and unloading are required. In addition, a large amount of magnesium is needed as a reducing agent, which increases the production costs. Therefore, low-cost continuous production of pure titanium
process has been the goal of people. Now new technology for the preparation of pure titanium are listed as following: high temperature solution phase of Mg reduction method, titanium tetrachloride electrolysis method, continuous liquid reduction method, flow continuous gas phase smelting method, direct electrolysis reduction of titanium dioxide\cite{4,5}. Titanium tetrachloride electrolysis method has developed rapidly and the researchers of United States, Japan, the former Soviet Union, Italy, France and China have carried out long-term tracking and in-depth research on this method. In 1953, Kroll, the founder of magnesiothermic reduction process, predicted that magnesiothermic reduction process would be replaced by titanium tetrachloride electrolysis 15 years later. In the United States, Dow-Hemet has built a plant to produce titanium sponge by titanium tetrachloride electrolysis. However, it is hard to control the reverse reaction between titanium and chlorine. Hence titanium tetrachloride electrolysis method has been in the laboratory research stage and cannot be applied in industry. And the Dow-Hemet Production lines was shut down. Another research hotspot is titanium dioxide electrolysis, also called FFC Cambridge process. It is a new method of preparing titanium sponge by electrolysis reduction of TiO2 in CaCl2 molten salt proposed by a professor in Cambridge university in 1998, and has been applied for patent. This method caused a stir for a time. British companies have developed corresponding production lines for experimental production. But up to now this method remains at the stage in laboratory and there are still many technical difficulties in its industrial production.

In order to reduce the cost of raw materials, the material researchers have taken many other effective measures on the premise of effectively reducing the extraction cost of titanium sponge. On the one hand, titanium alloy can be directly synthesized by chemical method from raw materials, instead of the preparation of titanium sponge. For example, using TiO2, Fe2O3, Al2O3 and MoO2, Ti-4.5Al-1.5Fe-6.8Mo alloy can be directly prepared by molten salt electrolysis \cite{6}. It has also been reported that TC4 alloy powder was prepared directly by chemical method using high titanium slag and intermediate alloy. Then the obtained TC4 powder can be formed directly by powder metallurgy. Although the purity and quality of the alloy obtained by above methods need to be further improved, this method has great potential with the development of the production process and the classification of application standards, which may become a mainstream method to produce of low-end titanium alloy if the cost of titanium sponge maintains a high level. On the other hand, revert materials can be reused to reduce production cost. In other words, raw materials which has been used will be valued at its most. In fact, the main reason for the high price of titanium products is the serious waste of waste material, especially in the field of aviation. For general aviation parts, the rate of finished products is about 10%. And for some complex thin-walled parts, the rate of finished products is only 5%. A lot of waste will be produced in the process of processing. Through the implementation of the relevant standards and process specifications, the technology of adding revert materials has become more mature. Most aircraft major force-bearing components and engine rotating parts have been allowed to produce by revert materials. Currently, more than 60% of titanium alloy products are added with revert materials in the field of American aviation. In the 1990s, there were five companies specializing in the production of waste material in the United States, such as IMT company, Timet company Morgan branch, etc., all of which have obtained aviation certification. IMT company is an important supplier of waste material for Timet company. The European Union established a recycling and smelting plant specializing in waste aerospace titanium alloy in the SAN giorgio of France in 2017, mainly for the aviation departments like Airbus. According to statistics, the cost of titanium alloy ingots can be reduced by 0.7% by adding every 1% revert titanium during smelting, and the addition of half of revert titanium can reduce the cost of titanium alloy ingots by more than a third. Thus, the reuse of revert titanium can significantly reduce the cost of titanium and titanium alloys. And the better way to reduce the cost of titanium alloy is to effectively use the revert material.
3. Alloy design
The core idea of low-cost titanium alloy design is to use cheap alloying elements to instead of expensive alloying elements without reducing the performance of the alloy. Lots of corresponding researches were carried out in the United States, Japan and other countries. Many low-cost titanium alloys have been developed\(^5\)\(^\text{-}^\text{10}\), showed by Tab. 1. As can be seen from Tab. 1, most of the cheap alloying elements, such as Fe, Fe-Mo, V-Fe, are used. Once the problem of smelting uniformity can be solved, Mo and V can be replaced by strong stable element Fe to strengthen alloy. Noted that Japan has made a comprehensive study of low-cost titanium alloy design in military, civilian, corrosion resistance, biomedical and other fields. Based on the foreign low-cost titanium alloy design ideas, researches on design and application of low-cost titanium alloys have been carried out in China. BAOTI Group has designed BTi-341, BTi-4111 and Ti-Al-Fe-Si alloy. These low-cost titanium alloys are added with Fe and mainly used in golf head, automobile exhaust system and other civil fields. Beijing Institute of Aeronautical Materials has designed Ti-Al-Mo-Cr-Zr low-cost titanium alloy for aviation. This alloy is widely used in the fields of aviation and marine for its good match of strength, plasticity and fracture toughness.

As a research and development institutions of new titanium alloy, Northwest Institute for Nonferrous Metal Research (NIN) has been at the leading level in the field of low-cost titanium alloy research and development. In 1984, NIN began to focus on the research on the low-cost titanium alloy Ti-451 alloy used in armor plate. The developed Ti-451 alloy plate has good mechanical properties and elastic resistance, and can reduce weight by 13% compared with the original armor steel. In the early 1990s, NIN studied on new low-cost titanium alloy Ti120 for light bulletproof clothing. Instead of CrMnSi, the bulletproof clothing made of Ti120 alloy can be reduced weight by more than 20%. During the Tenth Five-Year Plan Period, high-performance and low-cost titanium alloys Ti12LC\(^\text{[11]}\) and Ti8LC were developed by NIN using cheap Fe-Mo intermediate alloy, which was supported by the Foundation of National 863 Plan of China "High-performance and low-cost titanium alloy research"\(^\text{[12]}\). After alloy design, laboratory study and pilot scale development, the bar and plate with different specifications were prepared. Compared with TC4, the mechanical properties were better and the cost of its small size bar can be reduced by 30%. Now these alloys can be industrialized produced. Ti12LC tail nozzle and other typical components have been applied in the field of aviation. And Ti8LC and Ti12LC have been included in the national standard.

**Table 1 Low-cost titanium alloy for USA and Japan**

| Country | Alloy Designation | Chemical Composition [wt. %] | Low-cost features | Application |
|---------|------------------|------------------------------|------------------|-------------|
| USA     | Timetal-LCB      | Ti-4.5Fe-6.8Mo-1.5Al        | Replace the more expensive Ti-10V-2Fe-3Al alloy | Aerospace industry |
|         | Timetal 6-2S     | Ti-6Al-1.7Fe-0.1Si          | V is replaced by Fe in Ti-6Al-4V alloy, and the production cost of Ti-6Al-1.7Fe-0.1Si is reduced by 15% ~ 20% compared with Ti-6Al-4V. | Civil field requiring high strength |
|         | Timetal-125      | Ti-6Mo-6V-5.7Fe-2Al         | Use cheap Fe to improve processability. | Automotive filed |
|         | ATI 425          | Ti-4Al-2.5V-1.5Fe-0.25O     | Use cheap Fe and revert materials. | Armor plate and military vehicle parts |
|         | RMI RM           | Ti-6Al-4V-O                 | For Ti-6Al-4V alloy, titanium scrap is used to smelt the alloy. | Automotive filed |
|         | RMI VM           | Ti-6.4Al-1.2Fe              | V is replaced by Fe in Ti-6Al-4V alloy. | Armor and civil field |
| Japan   | Ti-Fe-O-N alloys | Fe, O and N are at most 2%, 0.6% and 0.1%, respectively. The total amount is no more than 2.5%. | Al is replaced O and N and V is replaced by Fe in Ti-6Al-4V alloy. | Civil field |

3
The technology of superplastic shaping and diffusion connection can be adopted below 800 °C to reduce the processing cost. Mo and V are replaced by Fe and Cr, respectively. The target alloy was Ti-6Al-4Pd Pd was replaced by O and N. Referring to Ti-0.15Pd, new titanium alloy is added Ru or reduced Pd, whose corrosion resistance has not decreased and cost is as same as pure titanium. Ce and La are added to improve machining performance. Titanium alloy with good cold working performance for automobile and eye frame.

Adding cheap alloy elements is the traditional method around the world. But the advantage of low-cost alloy design by adding cheap alloying elements is small because alloying elements of alloy account for a small proportion, which can only save about 5% of the cost. Therefore, it is better to design low-cost titanium alloy which is not sensitive to impurity elements and made with revert materials. Based on this research idea, the titanium alloy Ti5233 for armor plate with high efficiency and low cost was developed by NIN during the Eleventh Five-Year Plan Period. High quality protection factor and short process processing technology of Ti5322 armor plate was studied and low-cost preparation technology of the alloy was formed. As a high strength titanium alloy, the cost of Ti5322 is lower than TC4. Additionally, after heat treatment the room-temperature strength and elongation of Ti5322 plate (about 0.10mm~0.40mm) are 1050~1300MPa and 7%~14%, respectively. The quality protection factor of armor plate penetration of Ti5322 plate exceeds 1.8 and the protection safety angle reaches 28 degrees, which are all better than Ti-6Al-4V. Meanwhile, Ti5322 has excellent armor penetration protection ability. Therefore, Ti5322 potential to be promoted as an armor plate material. Since the 13th Five-Year Plan Period, Ti-532 and Ti-6432 have been developed by NIN which can be produced in compact processes for high efficiency fabrication and with adding revert materials. Ti-532 alloy, saving about 20% in cost, is superior to TC4 alloy in performance. And Ti-6432 cost can be reduced to half of that of TC4 alloy with revert materials adding. The research and development of these low-cost titanium alloys with different strengths and costs meet the application needs of aerospace, weapons, fighting vehicles and civil in China.

4. Processing and forming
Moreover, complex forming process, numerous procedures, strict requirement in technological process and high cost will account for the high price of titanium alloy products. For traditional titanium alloys, the manufacture cost is equal to that of raw materials. But for the difficult-to-deform titanium alloys, the manufacture cost is much higher. In addition, due to the large machining allowance, blanks formed by traditional way need to be machined out of a large amount of metal to form the final part, which increases amount of processing procedures and causes a huge waste of materials. Hence, according to different titanium alloy products, compact processes for high efficiency fabrication and the improvement of material utilization rate are another effective means to reduce cost [13]. At present, compact processes for high efficiency fabrication based on electron beam (EB) cold hearth smelting, which manufactures the plate, belt and tube of titanium alloys, is outstanding. Compared with traditional vacuum arc remelting, EB cold hearth smelting has prominent advantage as follows: ① High density and low density inclusions can be eliminated. Ingot with fine grains and uniform microstructure can be obtained; ② EB cold hearth have significant advantages in the recovery and smelting of revert materials, 100% of which
can be reused; ③ The ingot can be melted by one time. Flat ingot and hollow ingot can be produced and then sheet and pipe will be manufactured by less procedures.

At the end of 1980s, the technology of EB cold hearth was widely developed in the world, such as Germany, Japan, Britain, France, Ukraine. Glow discharge electron gun with cold cathode was investigated by Ukrainian which can be used in low-vacuum smelting. In Russia, EB cold hearths were also bought to let their titanium products enter the United States market. So far, the three major titanium companies in the United States have equipped themselves with EB cold hearths, and thus have an annual capacity of 35,000 tons. The United States took the lead in the research on the single smelting technology of EB cold hearth. TC4 ingot by single smelting can be directly rolled into plate, which was formed as AMS 6945 standard. At the same time, the researches on revert material recycling of titanium and titanium alloy by EB cold hearth have been carried out in United States, Russia and other countries. Now they have mastered the key technology of titanium alloy EB cold hearth smelting and obtained revert materials of multicomponent titanium alloys, which is suitable for industrial production. The products using revert titanium alloys produced by EB cold hearth smelting is mature and has widely applied for aviation and aerospace.

There exist considerable differentials between our country and foreign countries in the technology of EB cold hearth smelting. Qinghai Supower Titanium, BAOTI Group, Yunnan Titanium Industry, Luoyang Ship Material Research Institute, BAOSTEEL have already equipped with high-power EB cold hearth. In the EB cold hearth smelting process of multicomponent titanium alloy, alloy composition is hard to control because high vapor pressure alloying elements burn easily. Thus, EB cold hearth was mainly used for smelting and reverting pure titanium at the early stage. With advances in technology and needs in application, the tremendous progress in multielement alloy smelting has been made in China in recent years. As the initiator, Yunnan Titanium Industry united with other 19 enterprises to undertake one of the first key research and development projects in the 13th Five-Year Plan, which named “Development and application of manufacturing technology of low-cost and high-corrosion-resistant titanium alloy tubes and high-quality titanium strips”. Based on above project, compact processes for high efficiency fabrication based on EB cold hearth smelting has been developed. By this way, flat ingots can be melted directly and then processed into titanium strips, which significantly reduced the cost of titanium strip. Besides, the EB cold hearth smelting technology of TC4 has been studied by BAOTI Group and Luoyang Ship Material Research Institute. They can control the vaporization of trace elements effectively and produce up-to-standard TC4 flat ingots by industrialized manufacture. BAOTI Group has reverted and melted TA17, TC11 and other multicomponent titanium alloys. Now they have the industrial and large-scale production capacity [10].

In recent years, NIN and Qinghai Supower Titanium have researched on reverting and smelting of multicomponent titanium alloys. Qinghai Supower Titanium has a few EB cold hearths introduced from Ukrainian and the United States whose total power reaches up to 9300KW. The largest single ingot weight of nearly 20 tons. Qinghai Supower Titanium has the capacity to produce TC4 flat ingots for batch production using EB cold hearth for one time. Products of different batches are conformed to state standard. After the TC4 flat ingots were forged and rolled, the microstructure and properties had uniform stability and good consistency, which illustrates the advantages of property stability of multielement alloy ingots made by EB cold hearth [14]. NIN have researched on reverting and smelting of titanium alloys, such as TC4, TC11, TA10 and so on. The flat ingots, whose addition proportion of revert materials is more than 50%, meet national standard. Titanium alloy plate made by these flat ingots have been used successfully. Additionally, NIN and Qinghai Supower Titanium have melted multicomponent titanium alloys applied in aviation with EB cold hearth, which has been produced through experiments successfully. Further researches on forging manufacture and performance test are ongoing.

Noted that the two greatest advantages of EB cold hearth in the preparation of low-cost titanium alloy are smelting the blank directly and using high proportion of revert materials. It is believed that with the standards and application specifications being improved, EB cold hearth smelting of multicomponent titanium revert alloy and compact processes for high efficiency fabrication of slab will be the main
technique in the next 10-20 years to produce low-cost titanium, which is expected to be widely used in ships, weapons and combat vehicles.

Another important method to reduce the cost of titanium alloy is the near net forming technology, which can not only shorten the process procedures, but also improve the material utilization rate. In recent years, low-cost powder metallurgy technology has developed rapidly. It can directly produce alloy by mixing titanium powder with master alloy powder and then sintering at low temperature. By this way, the segregation of alloy composition can be effectively reduced and the coarse and uneven casting structure can be eliminated, and improve the properties of products. Products can be near net formed show good performances. This metal forming method also reduces resource and energy consumption. It is estimated that the cost of low-cost powder metallurgy technology can be reduced by about 50% compared with traditional preparation methods. The low-cost powder metallurgy technology will have a good application prospect in weapon and civil field in the future. Besides, superplastic forming/diffusion bonding, casting, laser melting deposition additive manufacturing etc. can shorten the process procedures and save costs.

5. Development tendency of Low-cost Titanium Alloys

New technology to produce titanium sponge

The cost of titanium material can be reduced fundamentally by solving the problem of extracting titanium sponge which is a problem that titanium alloy researchers need to solve for a long time. It is believed that with the development of science and technology being improved, low-cost titanium sponge extraction technology for industrialized manufacture will be developed and Ti will be removed from the rare metals in the future.

(2) Alloy powder preparation technology independent of titanium sponge production

If it is impossible to reduce the cost of titanium sponge, the method of directly synthesizing titanium alloy by using high titanium slag and master alloy through chemical method, instead of the extraction of pure titanium, will be another main method to product low-cost titanium alloy. A series of low-cost titanium alloys prepared by chemical methods may be developed. Chemical method is expected to be combined with the powder metallurgy method to significantly reduce the cost of low-end titanium alloy, which can be applied in the field of weapons and civil.

(3) EB cold hearth smelting technology of multicomponent titanium revert alloy

For now, EB cold hearth smelting technology of revert multicomponent titanium alloy combined with compact processes for high efficiency fabrication is expected to be applied to practice immediately. It is the first time that low-cost titanium alloy has been used in a real sense. According to the calculation, though revert material adding and compact processes of rolling, the cost of titanium alloy plate and plane forging can be reduced by more than 50%, and the ordinary TC4 alloy plate can be reduced to less than 100,000 yuan/ton. However, there are still some difficulties impeding the wide application of this technology as follows: ① A conventional low-cost titanium alloy is lacking, which should have a wide composition range, and can be prepared by adding more than 80% of different revert materials. ② It is hard to control component precisely during smelting process of multicomponent titanium alloy. Thus, it needs to solve the problem of composition control in multielement titanium alloy EB cold hearth smelting. ③According to different specifications, quality and revert materials, a classification management system should be established as soon as possible to ensure the reliability of raw materials.

(4) Establish the classification standards for low-cost titanium alloys used in different industries

As is known, the application of titanium alloys is mainly driven by aviation. All the current standards for titanium alloys are established according to aviation application. Whereas, in weapons, combat vehicles, civil and other fields, the standards of composition, ultrasonic examination and microstructure need not be so strict. The classification standards for titanium alloys used in different industries need to be established as early as possible. Only by establishing the corresponding classification standards, can the raw materials and preparation
process be pertinence, and can the low-cost preparation and application of titanium truly come true.

References
[1] Zhao Yongqing, Wei Jianfeng, Gao Zhanjun, et al. 2003 Materiials Reports 17(4) 5-7
[2] Zhu Zhishou, Shang Guoqiang, Wang Xinnan, et al. 2012 Titanium Industry Progress 29(6) 1-5
[3] Fritz Scholz 2010 Chem. Phy. Chem. 11 2078-2019
[4] Mo Wei 2008 Titanium (Beijing Metallurgical Industry Press)
[5] Zhang Wenyu 2011 Research progress of high-performance and low cost titanium alloy 5 74-79
[6] Du Jijiang, You Lei, Li Qingyu, et al. 2012 Rare Metal Materials and Engineering 41(12) 2191
[7] Wu Yinjiang, Duan Qingwen, Zhou Lian, et al. 2003 Advanced Materials Industry 2 11-15
[8] P E Markovsky, V I Bondarchuk, O M 2015 Materials Science and Engineering A 645 150-162
[9] L Bolzoni, E M Ruiz-Navas, E Gordo 2017 Materials Science and Engineering A 687 47-53
[10] Feng Quyuan, Tong Xuewen, Wang Jian, et al. 2017 Titanium Alloy 31(5) 128-133
[11] Hou Zhimin, Zhao Yongqing, Zhang Pengsheng, et al. 2014 Materials China 8 506-508
[12] Zhao Yongqing, Li Yuelu, Wu Huan, et al. 2004 Rare Metal 28(1) 66-69
[13] Emma Calvert, Brad Wynne, Nick Weston, et al. 2018 Journal of Materials Processing Tech. 254 158-170
[14] Tang Zenghui, Xin Shewei, Hong Quan, et al. 2018 Materials China 37(3) 520-525