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Recycling of Titanium and Its Alloys for Sustainable Development: An Overview

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Abstract—Sustainable development essentially is the protection of the environmental, financial, social and other resources for the future generations. It needs to be applied immediately to safeguard the available natural resources. Considering the importance, characteristics and limited resources among the ores, metals and alloys, titanium recycling has been selected for discussion in the present work. In present era, usage of titanium and its alloy has increased drastically in aerospace, aircrafts, marine, defense, energy and other industrial sectors due to its high strength to weight ratio, superior corrosion resistance and its ability to work at wide range of temperatures from cryogenic temperatures to moderately high temperatures etc. Worldwide production capacity of titanium has increased to around 2,00,000M.T/year. Whereas only 30% (approx.) of titanium is converted into finished product and almost 70% material goes to scrap. This alarming data calls for recycling of scrap as titanium is an expensive element and also its extraction from its ores is very much energy intensive. The prime objective of the present work is to explore the alternate resources for titanium. Available resources and different recycling techniques have been discussed in detail to suggest some viable alternative to natural resources and strengthen the sustainable development activities.

I. INTRODUCTION

Word 'scrap' evokes vision of some unwanted and discarded material which comes out from the raw material while finishing it. Titanium is the 22nd metal of periodic table and known as transition metal having 4.54 g/cm^3 density, which lies between steel and aluminum and its melting point is 1667^{o}C.It is extracted from the two primary sources Ilmenite and Rutile found in the earth crust[1]. There are significant deposits of titanium in the earth, which is spread over across the world. Utility of this magic metal is increasing day by day but the resources are limited. Another important aspect is almost 70 to 80% titanium goes to scrap while realizing the useful product [2].

Sources of titanium minerals/ ores cannot be enhanced, but there is a need to minimize the generation of scrap by going for near net shape production of mill products/ components and recycling of scrap, which will help in sustainability of this metal. Similar concept can be applied for other metals and alloys too. In 2008, almost 33,500 tons of titanium metal was recycled [3].

II. SOURCES OF TITANIUM

In the earth about 0.6% of total minerals is present in terms of titanium as Rutile (TiO_2) and Ilmenite ($FeTiO_3$) (Fig. 1).

Fig.1: Typical minerals of titanium [1]

Major Ilmenite Deposit Region : are Eastern Coast & Western Coast of Australia, Richards bay in South Africa, Eastern Coast of America, Kerala in India, Eastern & Southern Coast of Brazil[1] & some parts of Russia.

Major Rutile Deposit Region : are Eastern & Western Coast of Australia, Southwest Coast of Sierra Leone, Richards Bay in South Africa, Canada, China, India [1] and some parts of Russia. Titanium Rich Sands are mined in Florida and Virginia in United States [1] and in Kerala in India.

World Titanium Reserves : According to USGS (United States Geological Survey) (Fig. 2), Ilmenite accounts for 92% of the world's consumption of titanium minerals. World resources of Ilmenite and Rutile is almost more than 2 Billion Tonnes but identified reserves are only around 750 Million Tonnes[1-4].

World Titanium Concentrates Production : According to USGS and depicted in Fig. 3, the leading producers of titanium concentrates include South Africa (1.22 Million Metric Tonnes), Australia (1.39 Million Metric Tonnes), US (300,000 Metric Tonnes), China (950,000 Metric Tonnes), Canada (770,000 Metric Tonnes), India (266,000 Metric Tonnes) [4-5].

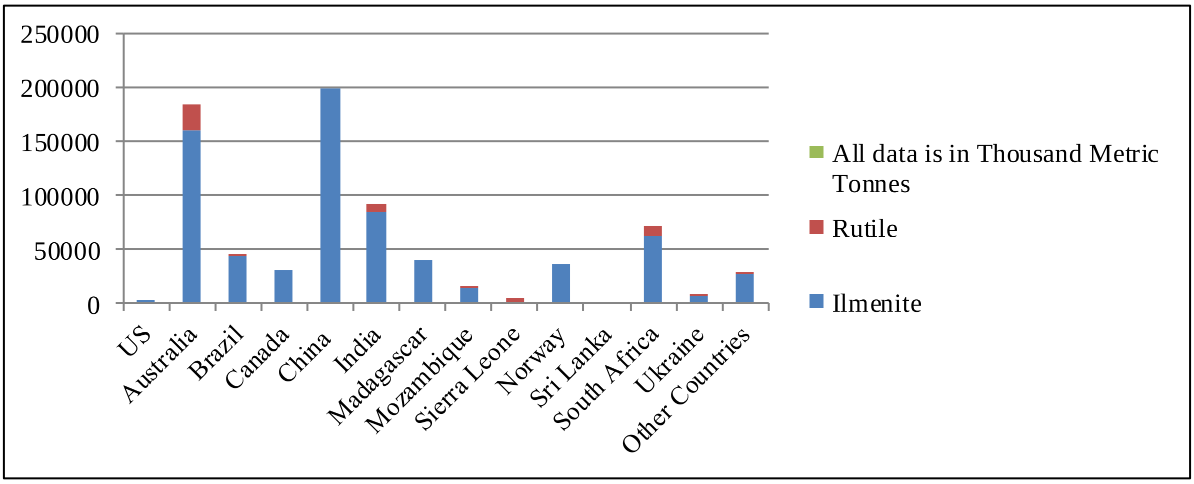

Fig. 2: World Titanium Reserve, Source USGS 2014 (except Russian resources)[4]

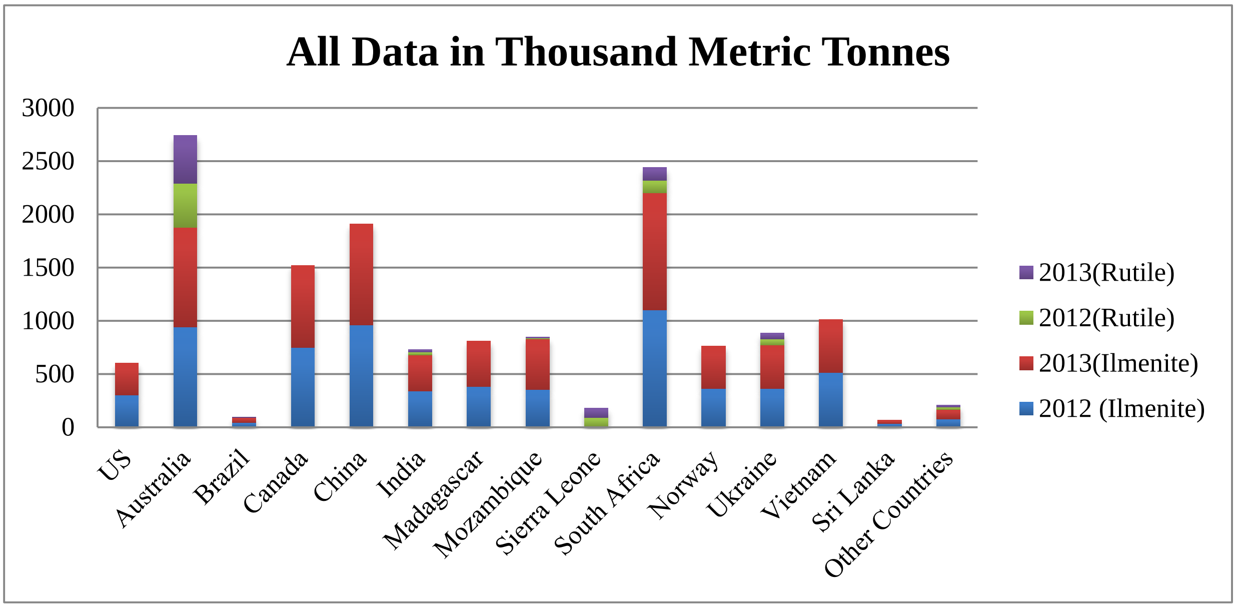

Fig. 3: World titanium production, Source USGS, 2014 [4]

World total production of Ilmenite and Rutile in 2012-13 was 13,290 (Thousand Metric Tonnes) and 1,500 (Thousand Metric Tonnes) respectively[1] excluding Russian production. Even though the production is very high in some countries, but still they import a large amount of titanium like as Russia and Japan [1]. According to VSMPO-Tirus, Russia, it has total capacity of 46,500 Metric Tonnes of titanium Sponge production per annum [6].

In India KMML (Kerala Minerals & Metals Ltd) is having world's first fully integrated plant and is the manufacturer of rutile based titanium by chloride process. Titanium dioxide is readily mined in its purest form from beach sand. The beaches of Sankarmangalam and nearby area in Kollam are rich in titanium metal. In 1909, a German scientist, discovered traces of monazite in the sand flakes of the imported coir from Sankarmangalam, India. The beaches with a wealth of rare earth minerals become the centre of scientific attraction and led to establishment of Kerala Minerals and Metals Limited (KMML). The mineral separation unit of KMML is engaged in the separation of Ilmenite, Rutile, Leucoxone, Monzite and Silliminite from the beach sand since then [7].

III. TITANIUM SCRAP GENERATION

Titanium processing generates a significant amount of scrap and only 30% of the titanium is used as finished product. This scrap needs to be recycled. Titanium scraps are generated in the form of turnings and bulk weldabales (billet, bars, plate trimmings, chips, etc.). The scrap when it comes from the production and fabrication of titanium components called "*New/Virgin Scrap"* and when it is comes from the used components like as ships, heat exchangers, aircrafts parts, etc. is called " *Old Scrap*"[8] are shown in Fig. 5. According to USGS report-2015, 50,000 Tonnes of scrap was recycled in 2014 by titanium industry and Titanium Pigment industry recycled around 1.31 Million Tonnes of titanium scrap [9].

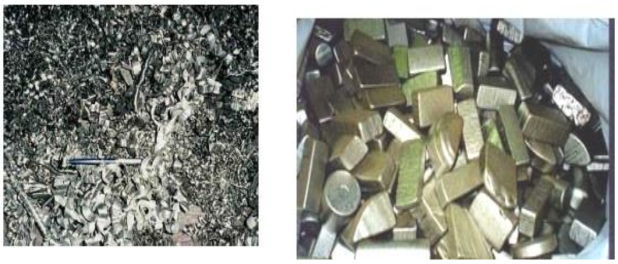

Fig. 5: Different Types of Titanium Scrap [10]

Only selected and classified scrap of titanium is recirculated and the contaminated & inhomogeneous scrap is downgraded to ferrotitanium production lines[11]. According to the Titanium industry sources estimation, the global titanium scrap market is almost 80,000 metric Tonnes for aerospace. Titanium scrap of similar amount is used in steel production[12]. Different types or grades of titanium scrap that are recycled to recover the pure titanium are given in Table 1[13] :

Table 1: Various grades of Ti scrap

Grade	Details
Mixed Titanium Solid	Clean sorted titanium solid scrap.
Titanium Turnings	Clean sorted titanium grindings or turnings.
Titanium Sworf	Assorted sworf and titanium residues.
Rutile Scrap	Titanium scrap consists of iron oxide materials.
Titanium Sponge/Residues	Assorted titanium in a sponge form.
Other Titanium Scrap	All other titanium scrap.

Fig. 6: Finished Product type titanium Scrap [14]

IV. RECYCLING TECHNIQUES & METHODS

Titanium recycling consists of converting titanium scrap into titanium ingot or pigment with or without virgin metal by using vacuum arc reduction or cold hearth melting practice or any other technique[15]. Titanium by-products can be recycled by melting or by hydrogenation[13].
According to Goldman Titanium the process of titanium scrap conversion into a ingot is as follows[14]:

- Crushing : To reduce the size of scrap.
- Cleaning : To remove all the oil & grease.
- Drying : To remove moisture from clean turnings.
- Magnetizing : To remove all magnetics.
- Screening : To sizes all clean turnings.
- Analysing : To check the chemistry of the product.
- Briquetting : Compact the turnings.

After these above steps the briquetted titanium scrap goes to the furnace for melting.
Titanium Scrap melting techniques are as follows :

A. Vacuum Arc Re-melting
B. Cold Hearth Re-melting
   - Electron Beam Cold Hearth Re-melting
   - Plasma Cold Hearth Melting
C. Induction Skull Melting

A. *Vacuum Arc Re-melting :* It is a secondary melting process for the production of metal ingots with chemical and mechanical homogeneity for the applications where high quality is required. In this type of melting process, initially the electrode is loaded into the furnace to be melted [16]. A schematic diagram of the process is shown in Fig. 7.

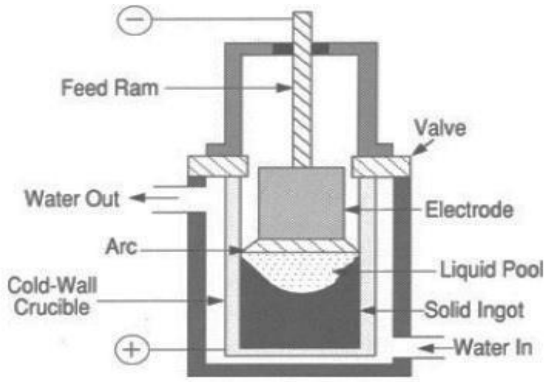

Fig.7:Schematic diagram of VAR process[17]

B. *Cold Hearth Re-melting :*Raw material is fed into one end of a water cooled copper hearth in which melting takes place. Then the molten metal is heated further as it flows across the hearth and is deposited in an ingot mold which is placed at the other end[18]. Cold Hearth Re-melting is further classified into :

- *Electron Beam Cold Hearth Re-melting :*In the electron beam cold hearth re-melting, one or more electron beam guns are used. In this type of process there is a cold hearth (may be more in number), one method to withdraw an ingot, one vacuum system having capacity up to 10^{-6} Torr and all these components are assembled in a housing as shown in Fig.8. This type of melting techniques are used to make primary electrodes, slabs, ingots from the scrap and fresh sponge. This is a effective method of melting by which the defects, which may arise due to inclusion will get eliminated due to step by step melting[17].

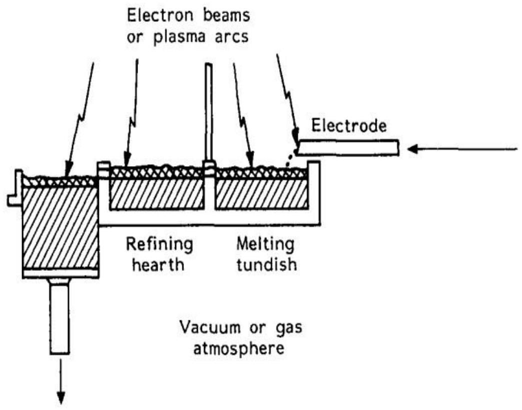

Fig. 8: Schematic diagram for EBCHM and PCHM[19]

- *Plasma Cold Hearth Melting :*In this method a transferred arc is produced in a swirl flow plasma torch[17]. Plasma arc furnace can be divided into three areas, first one is having a feed system, second one having the melting chamber & third is having a ingot chamber. The whole work is operated into a vacuum atmosphere to prevent the atmospheric contamination. Helium or argon gas is used to create the inert environment. In this method there are refining hearths by which the metals flows from one hearth to another hearth and finally reach the ingot. All hearths are made up of copper having water cooling jackets. Transferred arc plasma torches are used which provide the melting power. Then torch operates on argon or helium as the plasma gas as shown in Fig. 8[19]

C. *Induction Skull Melting :*In the induction skull melting method the melting takes place in the water cooled copper vessel, under vacuum or some controlled atmosphere [19]. No refractory lining is used in this method. A skull is formed under which it is melted to have cleaner melt[21].

V. DISCUSSION

All the materials are very precious due to their specific properties and therefore scarcely available. Once these resources are consumed, then further survival shall become difficult for future generations. So, it is the time to seriously think and decide about the sustainable development to protect the need of future generations. Titanium and its alloys are very precious due to their special properties and like any other material, there is an urgent need to recycle titanium. Several methods of recycling are available and the same has been discussed in previous section.

To initiate it, as a first step, large amount of titanium scrap is available, which are generated during processing. These scraps can be recycled, which will also save the energy requirements to melt the titanium ore as well as reduction in CO_2 emissions. As per reported data, 95.4% less CO_2 emissions takes place during the recycling of titanium to get 1 metric ton production [22]. So it is beneficial for us to recycle the titanium in terms of energy saving and also for the environment by lesser CO_2 emissions by which one can control the increasing temperature of earth due to global warming and also save the cost and energy required to produce fresh titanium because titanium made from scrap will be less expensive. As a general estimate, comparison on energy saving and reduction in greenhouse effect / CO_2 emission is presented in Fig. 9.

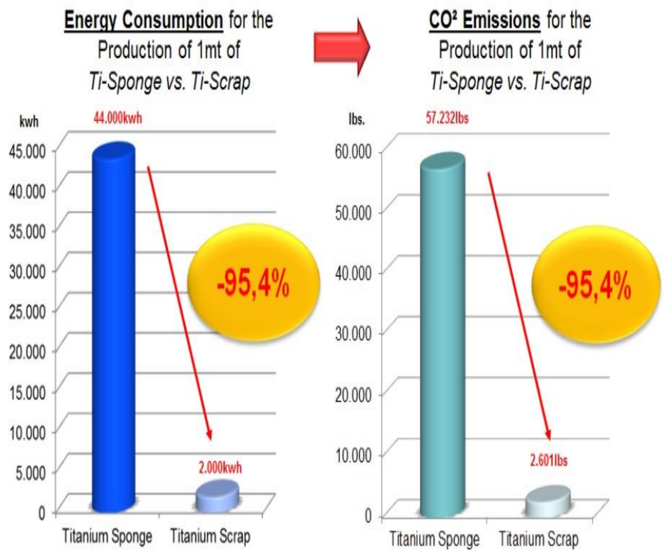

Fig. 9: Energy consumption & CO_2 emissions comparison[22]

SUMMARY

With the available data on resources of titanium and its recycling benefit, it can be clearly summarized that recycling of titanium is the need of the hour which will benefit not only by creating additional resource but also through saving of energy and reduction CO_2 emissions. Recycling titanium can also solve the issue of scrap handling. The old scrap can also be utilized to produce ferrotitanium by mixing titanium scrap with iron. This way it can contribute towards sustainable development.

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