A comparative corrosion study of titanium strips produced by wrought and direct powder rolling processes

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Abstract. Titanium is a light metal that has a high strength to weight ratio compared to steel. It has good corrosion resistance and is biocompatible. However, due to its high costs, its use has been limited mainly to the aerospace and medical industries. Direct powder rolling (DPR), a powder metallurgy (PM) method, is being developed with the aim of reducing the cost of producing titanium flat mill products. Critical to the success of the DPR produced products will be their ability to match or exceed the properties and performance behaviour of the equivalent products produced by wrought metallurgy. Titanium strips that are 89 % and 98 % dense were produced by DPR and their corrosion behaviour was compared to the wrought produced titanium strips. The corrosion tests were carried out in 1.75 wt.%, 2.0 wt.% and 3.5 wt.% NaCl solutions kept at 23 ºC using potentiodynamic polarization. The polarization curves showed that the wrought strips were the most corrosion resistant, followed by the DPR-98 % then the DPR-89 %. The influence of pores on the corrosion behaviour was high, therefore, effort needs to be made to reduce the pores of the DPR samples.

1. Introduction
Titanium (Ti) is generally known for its high strength and resistance to corrosion in a wide variety of environments [1] due to its ability to form a passive oxide film on its surface when exposed to oxidising environments. [2]. The corrosion resistance increases with the increasing thickness of the passive film [3]. Initially, titanium was predominantly used in the aerospace industry due to its light weight and high strength. Presently, due to its remarkable properties, titanium and titanium alloys have managed to pave their way into the petrochemical and power generation industries as condensers, heat exchangers [4],[5] and consumer products such as jewellery [6],[7]. Titanium products, though favourable, are considered very expensive due to raw materials and manufacturing costs [4],[7]. South Africa (SA) is the 2nd largest producer of ilmenite (FeTiO₃) which is the ore used to produce titanium. Nonetheless, SA does not produce any high-value semi-finished products such as Ti ingots, and/or mill products, powder etc. Mill products consist of plates, sheets, slabs, billets, bars, tubes and make up 75% of the global market share.

The Council for Scientific and Industrial Research (CSIR), through its Titanium Centre of Competence (TiCoC) in partnership with various universities, other science councils and private sector is mandated to add value to titanium through beneficiation of locally produced titanium ore in South Africa. This initiative involves the development of an innovative method of producing titanium metal
in powder form. Therefore, it is equally important to develop powder metallurgy (PM) processing techniques that can convert the produced titanium powder into high-value mill products, to test their properties and performance against the wrought commercial grade equivalent for various application environments. Direct powder rolling (DPR) of titanium powder is being developed mainly because the technique has the potential to offer cost benefits by reducing fabrication steps and has high material utilization [9]. The DPR process can be used to produce flat mill products such as strips, sheets and plates. The DPR process involves a roll compaction stage followed by a sintering stage or roll compaction followed by hot rolling and other subsequent finishing stages [10]. The objective of this paper was to compare the electrochemical corrosion behaviour of DPR produced titanium strips with the equivalent grade of wrought produced commercially pure (CP) Ti strips in a NaCl solutions

2. Experimental procedure

2.1 As received sample characterization

The developmental DPR strips were supplied by CSIR as Ti strips of different densities (Sample A-89 % and Sample B-98 %). The wrought strips (Sample C) were received from SAETRA (PTY) LTD as the supplier of ATI Mill product as CP Ti Grade 2 strips according to the ASTM B265.13A standard. The samples were sectioned and cut using water jet cutting. The samples were then hot mounted and prepared metallographically for microstructural analysis. The as-polished samples were etched with Kroll's reagent (46 ml distilled water + 3 ml nitric acid+ 1 ml hydrofluoric acid) for 5 seconds. The polished and etched surfaces were analysed on the Leica DMI 5000M optical microscope and image analysis was performed on the Olympus IMS software using the intercept method according to ASTM E112-13. Another set of samples were cut and the structural analysis was performed using the PANalytical X’Pert PRO X-ray diffraction (XRD) with a Cu-Kα diffractometer using λ = 1.54062 Å radiation at an accelerating voltage of 45 kV, a current of 40 mA. The samples were scanned at 20 from 20° to 120° angles at a scan rate of 0.0065.

2.2 Electrochemical testing

The 3.5 wt.%, 2 wt.% and 1.75 wt.% NaCl solutions were prepared using distilled water. The solutions were incubated at room temperature (23°C ± 1 °C) for 24 hours before the tests. Corrosion testing specimens were prepared by attaching a copper wire to a surface of the samples using an aluminum tape and cold mounted in resin. The exposed surface of the samples during potentiodynamic testing was 0.071 cm². The experiment was carried out according to ASTM G3-89 2010 by means of the electrochemical test conducted on the Autolab (NOVA version 2.1.0) potentiostat, with the electrolyte kept at room temperature (23°C ± 1 °C) using a thermostat controlled bath. A silver chloride electrode (Ag/AgCl) was used as the reference electrode (RE), graphite as the counter electrode (CE) and the samples as the working electrode (WE). The tests were conducted at a potential range of -1 V to +2 V at a scan rate of 5 mV/s. All measurements were carried out at least triplicated in deaerated solutions for the repeatability of data.

3. Results and discussion

3.1 XRD results

The structural analysis of samples is shown in figure 1. The XRD analysis confirms that the materials are unalloyed titanium, with a hexagonal structure with a = 2.9500 Å, b = 2.9500 Å and c = 4.6860 Å lattice parameters.
In order for the titanium strip to be classified as grade 2, it must meet the ASTM B265 standard for strips, sheets and plates. Table 1 gives the composition requirements for grade 2 according to the latest ASTM B265-15 standard. Based on the grading and compositional analysis provided by suppliers, both DPR and wrought samples were classified as titanium grade 2.

### 3.2 Composition of samples

**Table 1.** The composition of the grade 2 Ti samples according to suppliers.

|                  | Ti   | Fe  | O₂  | N₂  | C   | H₂  | Residuals |
|------------------|------|-----|-----|-----|-----|-----|-----------|
| DPR: Sample A-89\% (wt.\%) | bal  | -   | 0.22| 0.02| -   | -   | -         |
| DPR: Sample B-98\% (wt.\%) | bal  | -   | 0.24| 0.01| -   | -   | -         |
| Wrought ASTM B265-13a: Sample C (wt.\%) | bal  | 0.11| 0.10| 0.004| 0.1 | -   | -         |
| **ASTM B265-15: Ti grade 2 (wt.\%)** | **bal** | **≤0.30** | **≤0.25** | **≤0.03** | **≤0.08** | **≤0.015** | **≤0.3** |

3.3 Optical microscope results

The microstructures of the three titanium samples analysed using an optical microscope are shown in figure 2. From the optical microscope, it can be seen that sample A-89 % has the most pores followed by the sample B-98 % than the wrought sample C. The difference in the number of pores observed confirms the differences in the densities of the samples. After analysing the images, it was found that the pores in sample A-89 % occupy 6.8 % of the total area, pores in sample B-98 % occupy 2.6 % and sample C-wrought occupy a negligible value.

The images in figure 3 show the grains of all the samples. The DPR samples show large grains of approximately 52 μm and 60 μm average length for the DPR-89 % and DPR-98 % samples respectively (figure 3a and b). The wrought sample shows smaller equiaxed grains of approximately 27 μm average length (figure 3c).

3.4 Electrochemical results

Figure 4(a-c) shows the polarization curves of the samples in 1.75 wt.%, 2 wt.% and 3.5wt.% NaCl solutions respectively. All the curves show active (A), transmissive (T) and passive (P) regions. The titanium oxidation reaction is predominant in the active region. The oxide spreads over the entire surface suggesting the presence of a passive film. Figure 4a shows that DPR B-98 % and wrought CP Ti grade 2 are more corrosion resistant relative to the DPR A-89 % sample. The cathodic reactions of the samples are different, the wrought sample always shows a transmissive region. The tendency for
the transpassive behaviour increases with a decrease in porosity. All three potentiodynamic polarization curves show that the wrought sample gave better corrosion resistance to corrosion in the three concentrations of NaCl. The acceleration of the formation of the passive region depends on the chlorides concentration. The passive region forms readily in more concentrated solutions than in dilute concentrations [11].

![Micrographs](a) DPR A-89% (b) DPR B-98% and (c) wrought C produced samples.

Figure 2. Optical micrographs of a) DPR A-89% b) DPR B-98% and c) wrought C produced samples.

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Figure 3. Optical micrographs of a) DPR A-89% b) DPR B-98% and c) wrought C produced samples.

Figure 5a presents the values of the corrosion rates per year for all the samples in different NaCl solutions. The corrosion rates of the samples increase with increasing concentration of NaCl and the $i_{corr}$ of the samples increase with increasing concentration of NaCl, this is consistent with the known tendency of chloride ions to attack the surface [11]. Increasing the concentration of NaCl increases the chloride ion (Cl-) concentration which causes the partially protective film to break down and leads to the instability of the metal. The highest corrosion rate was found to be 2.2 mm/year for the DPR A-89% sample in 3.5 wt.% NaCl with the lowest being the wrought sample at 0.2 mm/year in the 1.75 wt.% NaCl. The general behaviour observed in Figure 5a is that the wrought C samples have a lower tendency to corrode, followed by the DPR B-98 % then the DPR A-89 %. The reason for this behaviour can be explained using the porosity of the three samples. Blackwood and Chooi [12] reported that the corrosion rate of porous titanium is significantly higher than that of highly compact titanium with little or no porosity. Although the non-ideal passive behaviour in porous samples has not been fully explained yet, Blackwood et al. [13] found that it may be related to the difference in electrode potential with the depth of the pores.

The grain size is considered to have an influence on the corrosion resistance of a material. However, the texture and number of pores have a higher effect of the corrosion behaviour than the grain size [14]. Hoseini et al. [14] investigated the effect of grain size and texture on the corrosion behaviour of CP Ti and found that the sample with larger grains was more corrosion resistant relative to a sample with smaller grains. The findings by Hoseini et al. [14] are applicable provided all the other factors such as porosity, composition etc. are constant. For this paper, other factors are not constant therefore it was difficult to study the effect of the grain size on the corrosion rate.
Figure 4. Potentiodynamic polarization curves for the samples in (a) 1.75 wt.%, (b) 2 wt.%, (c) 3.5 wt.% NaCl solutions.

Figure 5. The a) corrosion rates and b) current densities of DPR A-89 %, DPR B-98 % and wrought C samples.

4. Conclusions

According to metallurgical characterization and electrochemical results from the tests conducted, the following conclusions were made:

- The DPR B-98 % produced Ti grade 2 strips had better corrosion resistance compared to the DPR A-89 % dense strip. This shows that it is very critical that the DPR produces full density samples for corrosion applications.
• The wrought sample had a low corrosion rate compared to the two DPR produced Ti strips. Improvement of the porosity of the DPR samples is required in order to match or exceed the corrosion behaviour of the wrought sample.
• It can be concluded, therefore, that further work is required to reduce the porosity of the DPR produced strips to improve their density.

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