

Use of Titanium and Tungsten as an Alternative to Gold in Jewellery Manufacturing

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Abstract: In this study the use titanium and tungsten as alternatives to the noble metals in the jewellery industry was investigated. The degradation of titanium and tungsten were compared to that of gold, used as reference. Alternate immersion tests were performed in 3.5% sodium chloride and artificial perspiration. The metals' abrasion resistance with respect to textile fabrics was determined.

In general, there is around 30% difference in pit density for titanium and tungsten as compared to that of gold. Pit depth and pit diameter showed a similar trend. From the abrasive test performed, it was observed that titanium and tungsten had insignificant changes in the surface reflectivity with time. Hence, it was deduced that titanium and tungsten products would have longer maintenance intervals than that of gold. New tools and techniques, however, would be required by jewellers to work with titanium and tungsten.

Keywords: Gold, Titanium, Tungsten, Corrosion, Accelerated Tests, Pitting, Abrasion, Abrasive Test, Reflectivity, Jewellery.

1. INTRODUCTION

The exports in jewellery in Mauritius presently amount to around 100 million USD. However, only 28 jewellers, out of a total of over 500, are involved in this activity and there is, as a result, much room for developing this industry further in the country. It should be noted that the majority of the jewellers use only noble metals, that is, platinum, gold and silver, for manufacturing their products. With the rise in the price of the noble metals on the world market after the global financial crisis, jewellers at present cannot thrive without innovation and working differently. One of the avenues that could be adopted consists of using non-noble metals, such as titanium, tungsten and stainless steel as an alternative to the noble metals [1]. This will enable the jewellers to decrease the cost of their raw materials and, also, to develop products with new and innovative designs.

Presently, in Mauritius, stainless steel jewellery products are imported from other countries and those made of titanium and tungsten are manufactured locally, though, by very few jewellers. In a recent survey, it has been found that 65% of the jewellers do not intend to use alternative metals to gold in a near future [1].

The main reasons were that the jewellers do not possess the required knowledge to work with and use these metals [1]. Moreover, accurate information on the suitability of the use of these metals as jewellery is not readily available.

1.1. Gold

Gold is the most commonly used noble material in the jewellery sector in Mauritius. This is mainly due to its excellent machinability, workability, joinability and castability properties. This is also the case for the other noble metals, including silver and platinum, used in the industry.

Gold, however, abrades continuously during the time it is worn. Due to this abrasion, people wearing gold rings have a trace of gold almost everywhere [2]. For jewellery, abrasion of gold may happen due to friction with skin and friction with textile fabrics [3]. It should be noted that intentional rubbing of a gold ring on a quartz microfibre leads to an abrasion of up to 0.37 m gold. Apart from the loss of the material, scratches are also formed on the material's surface.

In addition to abrasive wear, gold faces would experience sweat-induced corrosion [2].

However, the impact of the later compared to that of the mechanical wear is reported to be negligible [2]. A simple immersion test performed in artificial sweat for two days has revealed that there was no weight loss of the metal [2].

The corrosion of gold has been studied for more than 50 years, still its understanding remains rather limited [4]. It should be noted that in the presence of chloride ions and other complexing agents like CN^- and Br^- , gold does corrode and this restricts its application in environments containing these species [4]. At sufficiently low potentials, gold anodically dissolves as Au(I) with the reaction rate being independent of pH for $\text{pH} > 1.5$. As the potential is increased, Au(III) forms [5].

1. 2. Titanium

Titanium offers elevated specific strength, high fatigue life, toughness and excellent resistance to corrosion in normal conditions [6]. It develops a very chemically stable, highly adherent, and continuous protective oxide film on the surface due to the metal's reactivity with oxygen. Hence, a surface oxide film forms spontaneously and instantly on its surface when it is exposed to air and/or moisture. Consequently, the oxide film has self-healing properties if it is damaged [7, 8, 9]. However, it has a very poor machinability. Its wear mechanisms with high speed steel and cemented carbide tools were identified as excessive cratering and deformation at the nose. It should however be noted that the tool wear mechanism changes with the cutting tool material, machining processes and processing conditions [10]. Cutting tools made of carbide inserts are suggested.

Titanium is one of the rare metals which is highly resistant to microbiological-induced corrosion (MIC) in seawater. This makes titanium a good candidate for its application in aircraft structural and engine parts, material for petrochemical plants and surgical implants. It is reported to provide immunity to both pitting corrosion and stress corrosion cracking in chloride solution [11]. Titanium alloys are, consequently, often the best choices for handling

halides and bleaches. They are considered to have far better resistance to these environments than the best 300 series stainless steels [12]. Consequently, titanium is used extensively in several industries including the chemical industries, desalination plants, aerospace industry and for medical applications. Titanium, however, exhibits poor corrosion resistance in some aggressive environments including high-temperature reducing acids and in crevices in hot chloride solutions [11, 13].

Titanium, however, has very poor tribological properties [14, 15, 16]. This is the reason why designers have tried to avoid its use in sliding systems. In situations where this is unavoidable, serious wear problems have been experienced [12].

Forming of titanium is also difficult since it exhibits a high degree of spring-back when cold formed. To overcome this problem, the metal should be either extremely over-formed or hot sized after cold forming [17]. Casting of titanium is also very difficult owing its high reactivity and high probability of contamination [17].

1. 3. Tungsten

Tungsten, on the other hand, have a high density, high strength at high temperatures, corrosion resistant, high elastic stiffness and good resistance to chemicals. It is a very brittle and hard material when pure. Tungsten has a very poor machinability. Because of its exceptional mechanical and thermal properties, it is extremely difficult to machine tungsten. Cutting tools made of carbide inserts are suggested. The cutting should be kept sharp at all times as extremely high shearing forces are required to cut tungsten. It is also very difficult to cast tungsten due to its high melting point. However, its main advantages are that it has a low thermal expansion, very close tolerances and fine finishes can be achieved.

Tungsten is considered to be highly corrosion resistant, especially in normal environments and it has been observed that it suffers no attack from the atmosphere at room temperature, or from hot or cold water. The corrosion resistance of tungsten alloys have been found to be lower than

pure tungsten. This has been attributed to the susceptibility of tungsten to form a highly protective oxide film upon anodic polarization in many aqueous media [18]. Tungsten also offers high corrosion resistance in acid media due to the low solubilities of the oxides in this media [18]. Several studies have been performed in which the dissolution rates for tungsten in sulphuric acid and sodium chloride were found to be negligible at 1 mA/cm² with the formation of a visible coating of WO₃[19]. The electrochemical characteristics of tungsten and its oxides have been extensively studied and are of significant technological interest. Many of its applications are in electrochromic field, photoelectrolysis of water, electro-machining and etching and the semi-conductor industry. However, much information is not available on the tribological behaviour of tungsten with most of the studies focusing on the properties of tungsten carbide.

Taking into consideration the needs of jewellers for diversifying their products and the specific properties of the non-noble metals, this study has been performed to investigate the degradation of titanium and tungsten as compared to gold, used as reference. Jewellery items are used in seawater while swimming and other seawater activities. They are kept permanently close to the body and are, thus, constantly subjected to degradation from perspiration. Also, they are intermittently in contact with textile fabrics leading to abrasion with time. To investigate these effects on the metals, alternate immersion tests in 3.5% sodium chloride solution was performed. The effect of artificial perspiration on the corrosion of the metals were analysed and their abrasion resistance with respect to textile fabrics was compared. The changes in manufacturing techniques that would be required for processing the non-noble metals, as compared to gold, were eventually discussed. The results are expected to give a clear insight on the suitability of using tungsten and titanium as alternatives to gold in jewellery manufacture.

2. METHODOLOGY

The following metal samples were considered

for the tests:

1. Gold – 18 carats, which consists of a minimum of 750.0 part of gold per thousand;
2. Titanium- Grade 1, manufactured according to ASTM B265 [20];
3. Tungsten- 99.95% min purity, manufactured according to ASTM B760 [21].

Small sample sizes of 40mm x 40mm were used due to high cost and difficulty in preparing the samples. To produce a proper finish on the metal surfaces for subsequent tests, they were ground and polished using 6µm diamond paste. A sample of titanium and that of tungsten is shown in Fig. 1.

In order to monitor the degradation of gold, titanium and tungsten in jewellery applications, the following methods were used:

1. To determine the behaviour of the metals in seawater environment, alternate immersion tests were performed according to ISO 11130[22]. Sodium chloride solution of concentration 3.5%wt, with a pH in the range of 6.0 to 7.0 was used. The temperature and humidity was also monitored. Sample sizes smaller than 50mm x 50mm x 0.2mm were, however, used. The corrosion testing was performed for 125 cycles. Micrographs of the surface of the tests specimens were taken at a magnification of X50 for every 25 cycles using a metallurgical microscope. The pit density was calculated. To facilitate

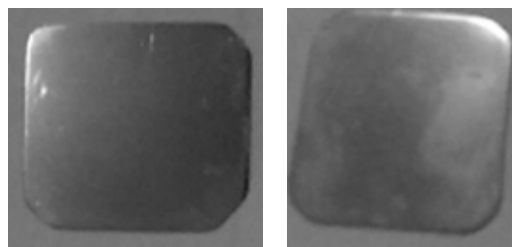


Fig. 1. Test specimens after lapping - Titanium (left) and Tungsten (right)

measurement of pit density, 3mm x 3mm grids were marked on the samples' surface. The pit shapes and diameter were noted at the end of the accelerated corrosion test at a magnification range of X200 to X500. Pit depth was determined at a magnification of X500 using the graduated fine-focusing knob of the microscope. The deepest and largest pits in each grid was used to calculate the average value of the respective properties over the whole surface of each sample. The changes in colour, pit density and sizes of pit and shapes were compared using the guidelines of ISO 11463 [23].

2. To determine the effect of perspiration on the selected metals, alternate immersion test were performed, using same conditions as in ISO 11130 [22], with artificial perspiration being used as the test solution. ISO 3160-2 [24] was used to prepare the solution of artificial perspiration. The same method as in (1) above was used to measure the changes in pit density and sizes of pit.
3. To test the abrasive effect of fabrics on the metal samples, the Martindale Taber Abraser was used. This apparatus is normally used to test the abrasion resistance of textile fabrics as per ASTM D4966 [25]. However, in this study, the abrasive effect of the textile fabrics on the metals was investigated. Hence, the equipment was modified for this purpose. A new holder, as shown in Fig. 2, was fabricated for holding the metal samples

which were rubbed against a standard abrasive fabric for a defined number of cycles under a load of 400g which was kept constant throughout the experiment, then their reflectivity was analysed using a spectrophotometer.

The initial reflectivity of the metal was measured and recorded using the spectrophotometer. The metal was then held using the new holder and mounted on the Taber Abraser apparatus. The surface was examined after 5000 hours intervals. The spectrophotometer was calibrated at 65 Degree observer. The size of its aperture was kept large and the wavelength used was 550 nm. It should be noted that changes in reflectivity of a surface is related to its surface roughness and surface finish [26].

Eventually, the changes that should be considered in the manufacturing processes in order to enable the Mauritian jewellers to work with the alternative metals were discussed.

3. RESULTS AND DISCUSSION

3.1. Alternate Immersion Test with 3.5% NaCl

It should be noted that most of the studies related to the corrosion of gold, titanium and tungsten have been performed through electrochemical tests. Alternate immersion tests have rarely been performed, though immersion tests have been reported. The results of the pit density observed on the metal samples for the accelerated corrosion test are shown in Fig. 3.

As expected, it can be observed that gold has a better corrosion resistance than titanium and tungsten. After 125 cycles, the pit density for titanium is 27% higher than that of gold and that of tungsten is 32% higher than that of gold. Titanium was, however, expected to show little or no corrosion at all. The alternate immersion tests can be considered as the nearest possible to the actual situations to which the metals would be exposed, especially during a visit to the seaside or while performing household tasks. These types of tests are presently rarely performed for the metals considered.

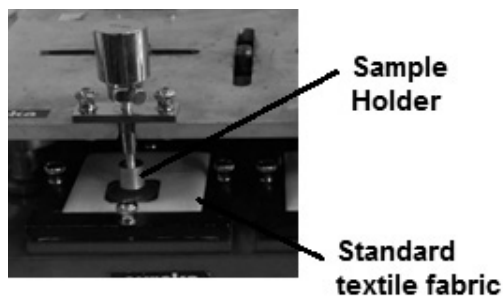


Fig. 2. Holder for the metal samples while used in the Martindale Taber Abraser

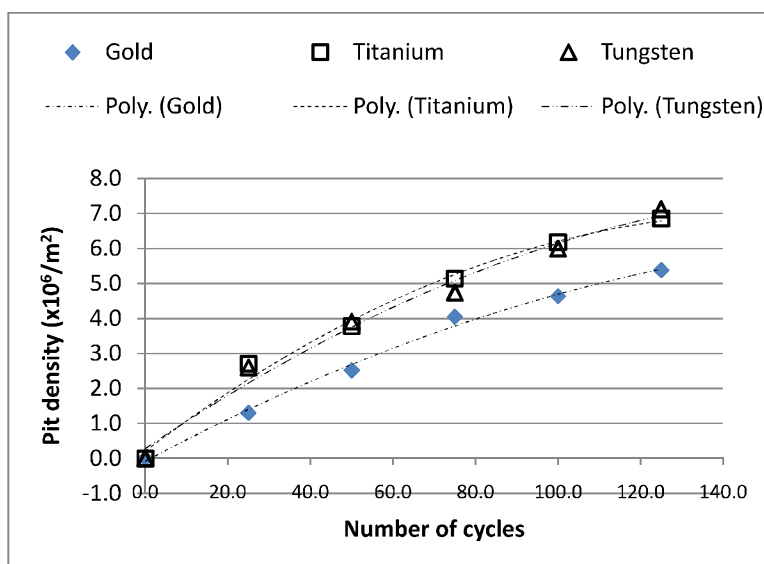


Fig. 3. Variation of pit density with number of cycles in the alternate immersion test.

The results clearly show that pits are formed at a higher rate for titanium and tungsten than that of gold. Though titanium has excellent corrosion resistance in seawater media, a few extensive studies [27-29] have demonstrated the susceptibility of titanium to corrode in a range of environments including acidic media, alkaline media and chlorides at different temperatures. For example, samples of sintered tungsten, with 90 to 97 wt% of tungsten and alloying additives of nickel, iron, copper and cobalt, was immersed in 5% sodium chloride solution for seven days. It was observed that their average corrosion rate ranged between 5 μ m/year to 13 μ /year. The corrosion rate was observed to remain fairly constant throughout the exposure period. An

average corrosion rate of 17-63 μ m/year in still seawater was obtained, where comparatively, the corrosion rate of mild steel is 127 μ m/year[30]. The pit density formation for tungsten was also found to be close to that of titanium, though the latter is also considered as a highly corrosion resistant material with very low corrosion rates in chlorides. This was based on electrochemical tests. The accelerated tests have not produced similar results.

The results for the depth and diameter of pits observed on the surfaces of the metals tested are shown in Table 1.

From the results, it can be observed that the main difference between the metals is related to the diameter of the pits observed. Though there is

Table 1. Results obtained after 125 cycles of alternate immersion test.

| | Average depth of largest pits (μ m) | Deepest pit (μ m) | Average diameter of largest pits (μ m) | Pit with the largest diameter (μ m) |
|----------|--|------------------------|---|--|
| Gold | 14 | 38 | 71 | 149 |
| Titanium | 15 | 36 | 64 | 289 |
| Tungsten | 18 | 82 | 122 | 323 |

a 30% difference in the average pit depth between gold and tungsten, the average diameter of pits for tungsten is 72% higher than that for gold. This may have a direct bearing on the appearance of the surface.

From the results obtained, it can be deduced that gold, as expected, offers a better resistance to pitting than titanium and tungsten. However, titanium may be a good alternative based on the results from the accelerated test with the pit density being only 25% higher and the depth and diameter of pits having little differences.

3. 2. Alternate Immersion Test with Artificial Perspiration

The results for the pit density on the metal samples for the accelerated immersion tests are shown in Fig. 4. The corrosion rate of titanium

and tungsten is 35% and 27%, respectively. For the artificial perspiration, titanium is the least corrosion resistant.

Referring to Table 2, it can be seen that the deepest pits have been observed on the tungsten samples. However, the average diameter of the largest pits was smallest for the gold samples. That for titanium and tungsten was 33% and 15% respectively higher than that of gold.

It can also be deduced that the 3.5% sodium chloride solution led to the formation of larger pits with a higher pit density than that of artificial perspiration. In fact, as pointed out by G. Stainhauser [2], sweat-corrosion has a minor impact in the corrosion of gold jewellery products.

It should be noted that, as shown in Fig. 5, the pits formed on gold samples are of irregular shape. Those observed on titanium and tungsten surfaces are more circular in shape.

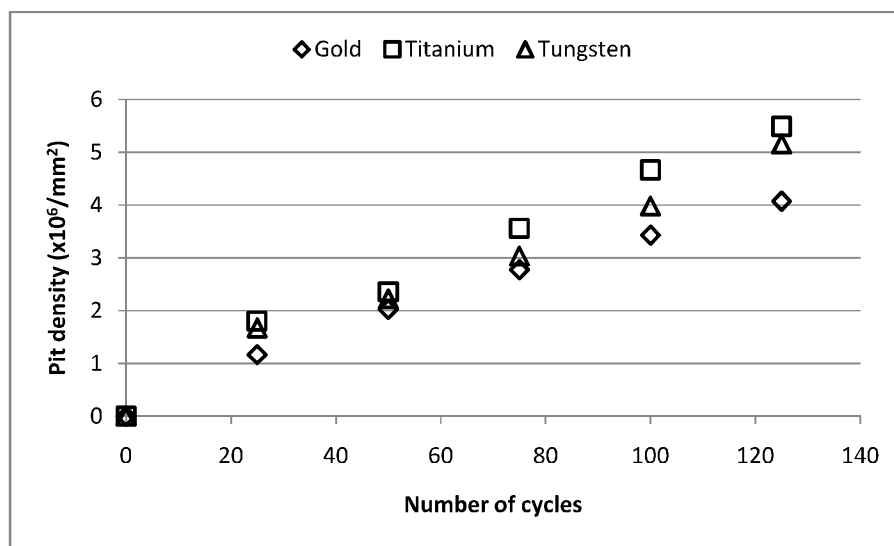


Fig. 4. Results of pit density against number of cycles for alternate immersion with artificial perspiration.

Table 2. Results obtained after 125 cycles of alternate immersion test in artificial perspiration

| | Average depth of largest pits (µm) | Deepest pit (µm) | Average diameter of largest pits (µm) | Pit with the largest diameter (µm) |
|----------|------------------------------------|------------------|---------------------------------------|------------------------------------|
| Gold | 14 | 24 | 39 | 160 |
| Titanium | 14 | 31 | 52 | 137 |
| Tungsten | 22 | 54 | 45 | 133 |

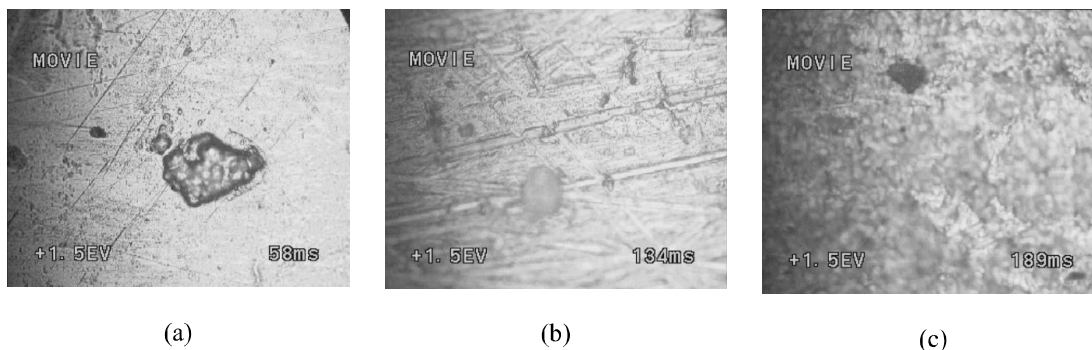


Fig. 5. Typical micrographs (with magnification of X200) of pits formed on (a) gold (b) titanium (c) tungsten samples

3. 3. Abrasive Effect of Fabrics

It can be observed that gold has a better reflectivity at the start of the tests. However, as expected, it abrades more easily than titanium and tungsten and after 30000 cycles, it's reflectivity decreases very close to that of titanium and tungsten.

Gold samples are more easily polished compared to tungsten and titanium based on the hardness properties of the materials. From Fig. 6, it can be observed that the higher reflectivity of the gold samples drastically decreased from

90.5% to 51.3% in 30000 cycles. The reflectivity for tungsten and titanium decreased insignificantly. This could be explained by the fact that titanium and tungsten are much harder materials than gold. Titanium may have poor tribological properties for industrial applications in sliding applications, however, these types of situations would not be relevant in jewellery applications. In the experiment, the metals have been rubbed with standard abrasive textile fabrics which provide a softer surface, hence less harsh conditions than in industry. It could be deduced that though titanium and tungsten would be more

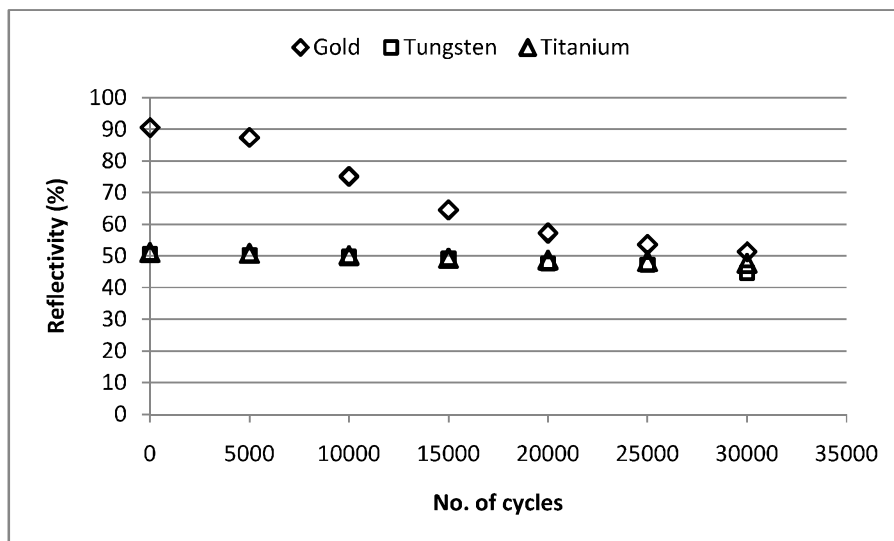


Fig. 6. Reflectivity of abraded metal samples

difficult to polish, their reflectivity would change insignificantly for a much longer period of use than that of gold.

3. 4. Manufacturing Techniques

The commonly used manufacturing processes by jewellers, who use essentially noble metals as raw materials, are casting, carving, cutting, engraving, forming, polishing, soldering and stamping. For them, significant changes would be required in the manufacturing techniques for the use of titanium and tungsten as materials in jewellery making.

Though, high speed steel tools may be used to machine titanium, this may lead to excessive wear. Titanium is a bad conductor of heat. Heat generated during cutting doesn't dissipate through the part and machine structure, but concentrates in the cutting area. The high temperatures that can be reached which can lead to cutting edge chipping and deformation, and dull edges on tools generate even more heat and further reduce tool life. The high temperature generated during the cutting process also causes a work hardening phenomenon that affects the surface integrity of titanium, and could lead to geometric inaccuracies in the part and severe reduction in its fatigue strength. Under these circumstances, cemented carbide tools would be a better alternative [10].

Forming titanium may be more difficult than that for the noble metals, taking into consideration its specific properties, such as strength to weight ratio and its tendency to spring-back. Hence, the metal needs to be extensively over-formed or hot sized after cold forming. Stress-relief operations need to be conducted after cold forming [30]. Other alternatives may be envisaged. Firstly, hot forming may be more appropriate. Secondly, thinner sections may be used for ease of cutting and forming. Thirdly, it would be easier to work with the metals available in finished forms. For example, rings can be made by cutting a proper diameter pipe to its required width and subsequently machining and forming it.

Though thin sheets of titanium may be easily sheared, as its thickness increases dimensional

accuracy may decrease and other problems such as cracking may result. It can be, more appropriately, cut to the required design using non-conventional machining methods such as jet or abrasive jet machining, especially when intricate shapes need to be formed out of the metal.

Tungsten is very difficult to machine since it is very hard and brittle at normal temperatures so that it is virtually impossible by normal methods to work with, especially for parts requiring intricate shapes and close tolerances. Though tungsten can be fabricated into many simple shapes and configurations, including bending, shearing, punching, riveting, it requires special handling and skill beyond that necessary for most metals and alloys since it is a strong, hard, crack-sensitive metal that is usually brittle at room temperature. Otherwise, it will generally result in cracked or laminated parts. Hence, tungsten, should be mostly used for applications requiring simpler machining methods, such as pendants.

Though working with titanium and tungsten as raw materials would require new techniques and new tools for processing these materials through non-conventional machining methods or other conventional machining and forming techniques, the use of these metals can lead to innovative and inventive designs so as to create new and fashionable products with greater added value.

4. CONCLUSION

Accelerated tests and abrasive tests were performed on titanium and tungsten with gold used as reference to observe the degradation of the metals in these conditions. As expected, gold offers the greatest resistance to corrosion, as observed with the accelerated tests. In general, there is around 30% difference in pit density for titanium and tungsten as compared to gold. Pit depth and pit diameter were also measured and compared. A similar trend was observed. Sweat corrosion is, however, not considered as main factor influencing material selection. Moreover, a 30% difference, with respect to the corrosion resistance of gold, is not expected to lead to serious effects on the surface appearance of the metals.

For the abrasive test performed on the metals, it was observed that titanium and tungsten would have insignificant changes in the surface reflectivity with time. The reflectivity of gold would, however, decrease significantly during the same time. Hence, titanium and tungsten products would have longer maintenance free periods and would need lesser amount of polishing, than those made of gold, during the lifetime of the product.

However, jewellers in Mauritius mostly use conventional machining and generally make use of conventional methods of production. Taking into consideration the specific properties of the non-noble metals, it would be difficult to use them without making some fundamental changes in their product design and production processes. It should be concluded that titanium and tungsten may become good alternatives to gold and other noble metals in the jewellery sector. Though the gold market will continue to prosper worldwide, most jewellers, using mostly noble metals, will face problems. Use of non-noble metals such as titanium and tungsten will allow them to thrive through innovation.

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