

“Effect of corrosion on abrasive wear in a range of materials”

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Engineering components, such as those which are employed in fluid sealing systems, experience abrasive wear deterioration, which is often significantly enhanced by corrosion processes and the interaction of corrosion with the mechanical damage. Broader understanding and quantification of the corrosive abrasion is appropriate to combat this complex degradation phenomenon. This paper discusses the influence of corrosion on abrasive wear and utilises a recently developed experimental technique which enables the quantification of corrosive abrasion damage of materials subjected to impingement by a saline aqueous solution containing suspended sand particles. The materials reviewed in this study were Zirconia, a Diamond-Like Carbon (DLC) Coating, High Velocity Oxygen Fuel (HVOF) WC-12Co, HVOF WC-10Ni, medium carbon steel (UNS G10400) and martensitic stainless steel (UNS S42000). UNS S31600 was used as a comparator material. The influence of acidic conditions was also investigated on the tribo-corrosion resistance of the martensitic stainless steel. Volume loss ratios, microscopy and surface roughness measurements were employed to expand the assessment of corrosion abrasion damage. The ceramic (Zirconia and DLC coating) and cermet (HVOF WC-12Co and HVOF WC-10Ni) materials exhibited excellent abrasion resistance, however, the cermets suffered extensively from corrosion related damage. The engineering steels, on the other hand, were extensively attacked by corrosion abrasion wear. Through this comparative study, material considerations, associated with the different mechanisms that occur in fluid seals, were also formulated.

1. INTRODUCTION

Mechanical seals are required to prevent leakage in engineering systems such as pumps and rotating equipment, however seals are allowed to leak within some degree, excess of this limit would be deemed as a failure. Wear due to abrasive particles suspended in the sealed fluid is a material deterioration mechanism which often leads to increases in leakage [1–3]. Wear occurs as the particles abrade the sealing faces and roughens the surface which subsequently causes an increase in leakage rates [4-5]. This roughening event can occur in even a short period of operation. Aqueous fluids with corrosive media (i.e. NaCl and/or low pH) also introduce corrosion into the degradation process which may enhance the overall wear [6].

Work has been conducted to comprehend the principle mechanisms of corrosion [7-8] and abrasion [9-10] in separate testing apparatus. Studies in recent years have attempted to assess the combined damage of both mechanisms when they interact with each other. Some papers argue that there is a reduction in wear when corrosive abrasion occurs [11-12]. This reduction in wear has been found in three-body abrasion testing machines (pin on disk and rubber wheel) which have found that the aqueous solution acts as a lubricant and hence reduces the friction between the substrate and counterface. Other researchers have reported that the aqueous solution does cause an increase in wear [13-15]. This was found on a variety of testing apparatus (thrust washer, fixed-ball micro-abrasion and impinging jet machines). A possible explanation for this are; the passive film breaks down due to the impact of abrasive particles, therefore, the exposed area of the material increases with surface roughening which accelerates corrosion rates leading to additional material removal (corrosion product) by the abrasive particles. Despite these studies, the material failure is still not completely understood as the combined effects of these mechanisms are complex.

What is clear is that material selection is a major factor which will influence the damage induced by corrosive abrasion. For mechanical seals experiencing aqueous fluid streams, stainless steel alloys are commonly selected as the most attractive candidates, however, in more corrosive medias and/or when abrasive particles are involved, high grade duplex stainless steels, high chromium cast irons and tungsten carbide cermets are preferred [16-18]. Steels tested in an impinging jet apparatus have been studied extensively in the past. Corrosive abrasion has contributed significantly to the overall material loss of steels due to the breakdown of the passive film leading to higher corrosion rates [19-20]. The damage has been shown as a form of pitting with directionality of the flow particles [21]. Studies have also assessed tungsten carbide cermets in both dry and wet abrasion tests. In dry conditions, material loss of cermets has been found to be due to the preferential removal of the soft metallic binder which results in the tungsten carbide particles fracturing/spalling caused by the decrease in adhesion [22-23]. This was also found to be the case in wet conditions, plastic deformation/micro-ploughing caused removal of the binder which resulted in fracture and fragmentation of the carbide grains as well as cracking between grains [24-25].

This paper will evaluate the effects of corrosion on sliding abrasion by utilising a new technique [19] which quantifies corrosive abrasion damage of materials subjected to a submerged impinging aqueous jet with suspended silica sand particles. A wide range of materials was studied in different testing conditions. This considered the effects of corrosion on sliding abrasion for materials which are susceptible to corrosion (engineering steels and HVOF sprayed coatings) and also the pure mechanical sliding abrasion damage for materials which are immune to corrosion (ceramics).

2. METHODOLOGY AND MATERIALS

Corrosive abrasion has been assessed by using a new approach which was recently developed by the authors. Utilising a recirculating impingement rig, described elsewhere [26], the mechanical deterioration processes (impingement erosion and sliding abrasion) along with the electrochemical damage and additional material loss involving interactions between corrosion and mechanical effects, also termed as synergy, can be quantified. The idea behind this new technique is the understanding of the

fluid mechanics and the material degradation processes that are involved on the test material surface under solid/liquid impingement, as shown in Figure 1.

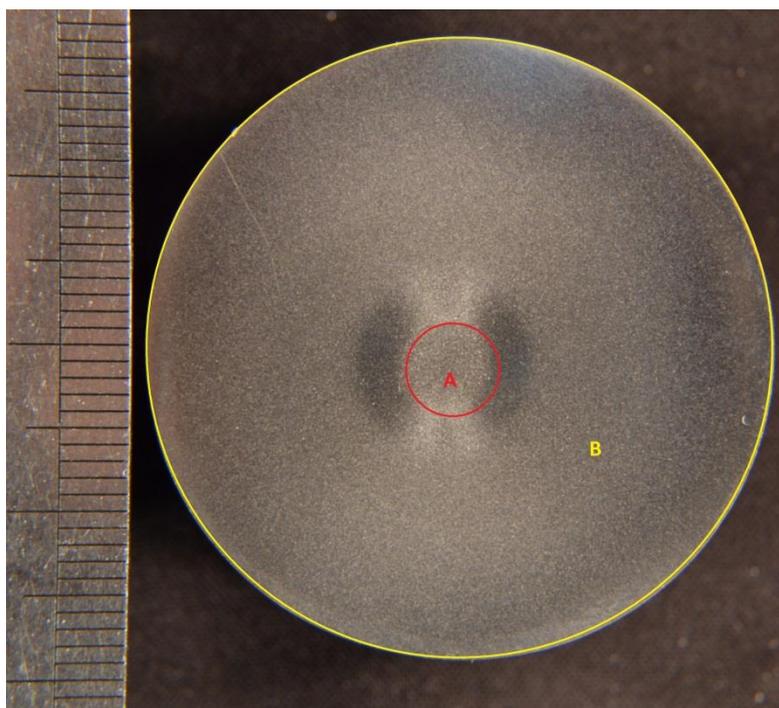


Figure 1: Post-test surface of the UNS S31600 reference specimen

Area A represents the surface region directly underneath the jet, also referred to as the wear scar, where erosion, corrosion and synergy simultaneously occur. Area B illustrates the outer region, adjacent to the wear scar, in which sliding abrasion, corrosion and synergy take place due to the low angle of impingement. The sliding abrasion damage is induced by the action of the sand particles sliding along the surface of Area B after they have impacted on Area A. Through mass loss measurements, the total effect of the above mechanisms is distinguished. Surface topography is utilised to define the volume lost inside the wear scar and in this way it can be isolated from the outer area which is the main focus of this paper. Impressed current cathodic protection was also employed, by keeping the electrode potential of the specimen at -0.85V (Ag/AgCl reference electrode), to segregate the mechanical damage (sliding abrasion) from corrosion and synergy.

All the material coupons were round with 38mm diameter. The chemical composition of the materials is shown in **Error! Reference source not found.1**. The macrohardness tests were conducted on a Vickers MAT31 hardness machine. Roughness measurements in the outer area of specimens were conducted with a SV-2000 2D surface profilometer. The metallic materials were ground to surface finish of 0.07 μ m Ra value; all other materials were tested in the as-received condition. Table 2 demonstrates density, bulk hardness and initial roughness values of each material. Figure 2 demonstrates the sand size of the two types of sand particles according to the sieving results. The hardness of both types of silica particles are 7 Mohs, or 1,160HV in Vickers terms. As the densities of the materials and the testing conditions (Table 3) vary in this study, volume losses of the tested material and the reference material (UNS S31600) were utilised as an appropriate performance assessment. An example of how the volume loss ratios are distinguished is shown in Table 4. An Olympus GX-51light microscope and a Hitachi SU-6600 field emission scanning electron microscope were employed for the post-test surface examination.

Table 1: Chemical composition of test materials

Material	C%	ZrO ₂ %	WC%	Ni%	Co%	Cr%	S%	Mn%	Si%
Zirconia	-	100	-	-	-	-	-	-	-
DLC coating	100	-	-	-	-	-	-	-	-
HVOF sprayed WC-12Co	-	-	88	-	12	-	-	-	-
HVOF sprayed WC-10Ni	-	-	90	10	-	-	-	-	-
UNS G10400	0.40	-	-	-	-	-	0.05	0.75	-
UNS S42000	<0.15	-	-	-	-	13	<0.03	<1	<1

Table 2: Density, hardness and initial roughness values of the materials under this study

Material	Density (g/cm ³)	Bulk Hardness (HV)	Initial Roughness (µm Ra)
Zirconia	5.60	1,050*	0.37
Diamond-Like Carbon (DLC) Coating	2.70	3,500*	0.07
HVOF WC-12Co	14.82	1,100 (20kgf)	0.37
HVOF WC-10Ni	14.96	1,000 (20kgf)	0.36
Medium carbon steel (UNS G10400)	7.85	240 (5kgf)	0.07
Martensitic stainless steel (UNS S42000)	7.75	280 (5kgf)	0.07

*According to the supplier's specification

Table 3: List of the materials and their solid/liquid impingement testing conditions

Material	Testing conditions				
	Velocity	Temperature	Sand type	Sand concentration	Test duration
Zirconia	19 m/s	13°C-23°C	Rounded silica	150mg/L	1h
DLC Coating	18 m/s	40 ± 1 °C	Rounded silica	550mg/L	1h
HVOF WC-12Co	17 m/s	39 ± 1 °C	Sub-angular silica	200 ± 20mg/L	2h
HVOF WC-10Ni					
UNS G10400	19m/s	30°C-36°C	Rounded silica	150mg/L	1h
UNS S42000 pH=7	21m/s	43 ± 2 °C	Sub-angular silica	500mg/L	1h
UNS S42000 pH=3	21m/s	43 ± 2 °C	Sub-angular silica	500mg/L	1h

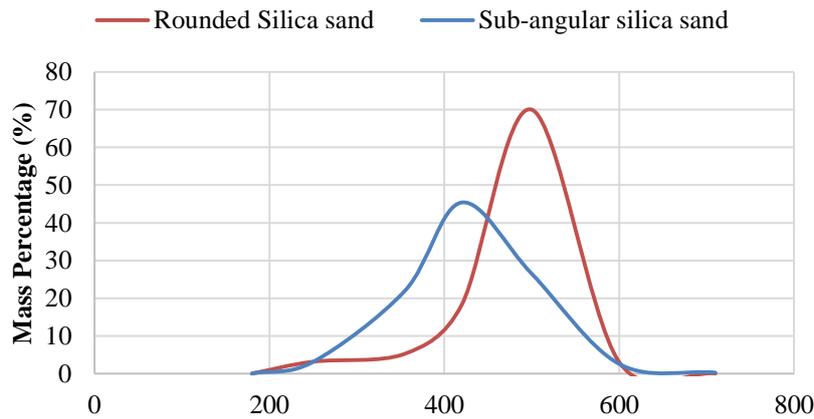


Figure 2: The size distribution of the two types of sand that were involved in this study

Table 4: An example of the calculation used to determine the performance ratio

	Total volume loss in the outer area (mm ³)	Volume loss due to sliding abrasion (mm ³)	Volume loss due to corrosion and synergy (mm ³)
UNS G10400	0.99	0.33	0.67
UNS S31600	0.35	0.21	0.14
Volume Loss ratio	2.83	1.57	4.79

3. RESULTS & DISCUSSION

3.1 Volume loss ratios

Table 5 illustrates the volume loss measurements relative to the reference material, termed as volume loss ratios. The volume loss ratio for the outer region of the material coupons is divided into volume loss ratios for sliding abrasion and corrosion and synergy. The ceramics exhibited superior corrosion abrasion resistance in comparison with the other comparative materials, and this is attributed to the absence of corrosion. It was evident that the presence of the corrosion related component on the other comparative materials enhanced the rates of corrosion abrasion and in most cases quite substantially.

Table 5: Volume loss ratios along with contributions of the two distinct degradation mechanisms

	Materials	Outer Area	Sliding Abrasion	Corrosion and Synergy
Ceramics	Zirconia [21]	0.03	0.05	0.00
	DLC coating	0.22	0.24	0.00
Cermets	HVOF WC-12Co	2.67	0.05	152.00
	HVOF WC-10Ni	0.64	0.05	34.00
Steels	UNS G10400 [19]	2.83	1.57	4.79
	UNS S42000 pH = 7	0.82	0.77	2.10
	UNS S42000 pH = 3	2.10	0.77	58.8

Red: Poor (>1.00) Green: Good (<1.00)

Error! Reference source not found. illustrates the percentage of the different degradation mechanisms occurring during corrosion-abrasion tests. According to the proportion of the overall damage, it is clear that the degradation of the ceramic materials (i.e. Zirconia and DLC coating) is mechanically dominated. The HVOF sprayed cermets along with the medium carbon steel, have been deteriorated extensively by the corrosion related component with the mechanical abrasion contribution to the overall damage as low as 5% (i.e. HVOF WC-12Co). In neutral conditions, sliding abrasion was the major degradation mechanism for the martensitic stainless steel. However, the behaviour of the martensitic stainless steel changed with the decrease of the pH, by switching the dominant deterioration process from mechanical abrasion to corrosion and synergy.

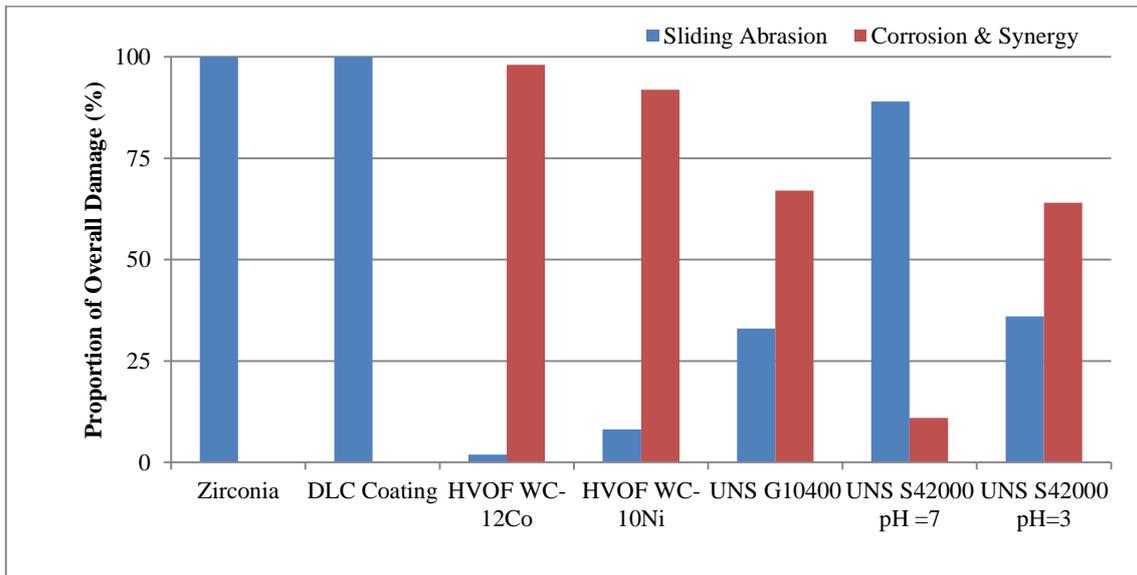


Figure 3: Proportions of overall damage for all tested materials

3.2 Microscopic images

Figure 4 shows the minor amount of damage which the ceramic materials experience as there was limited evidence of sliding abrasion damage. A small amount of scratches were found post-test on the DLC coating but it is unclear whether these were a result of sliding abrasion damage. The observed scratches on the Zirconia specimen were present before testing.

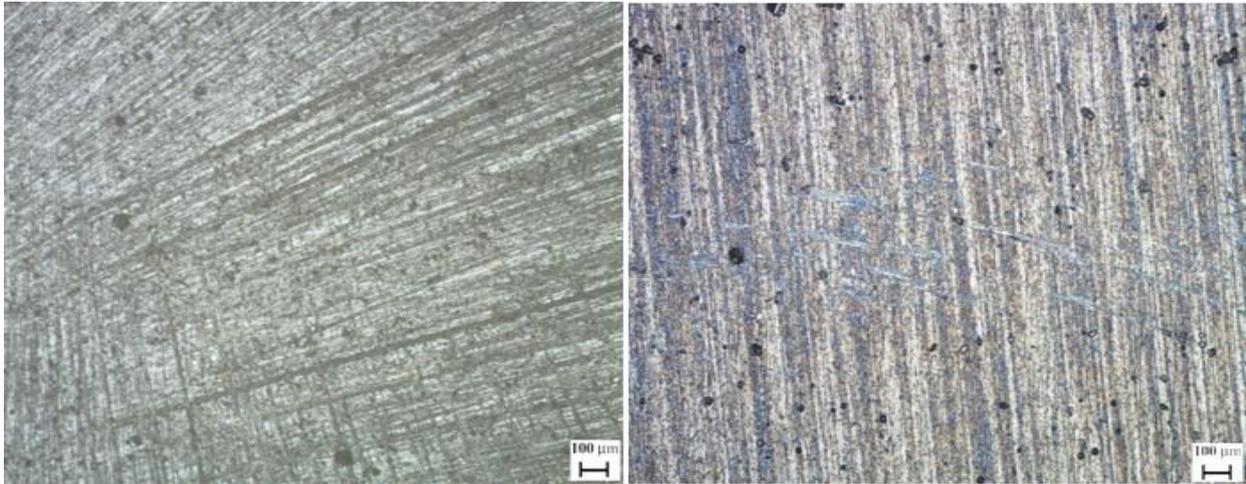


Figure 4: Zirconia (Left); DLC coating (Right) under free corrosion abrasion (FCA) conditions

Figure 5 shows the effect of cathodic protection on the HVOF WC-12 Co cermet. The microstructure after FCA testing depicts dissolution of the Co binder which has left the WC grains behind. However, by applying cathodic protection, the Co binder is not corroding away, and it does provide mechanical support to the WC grains.

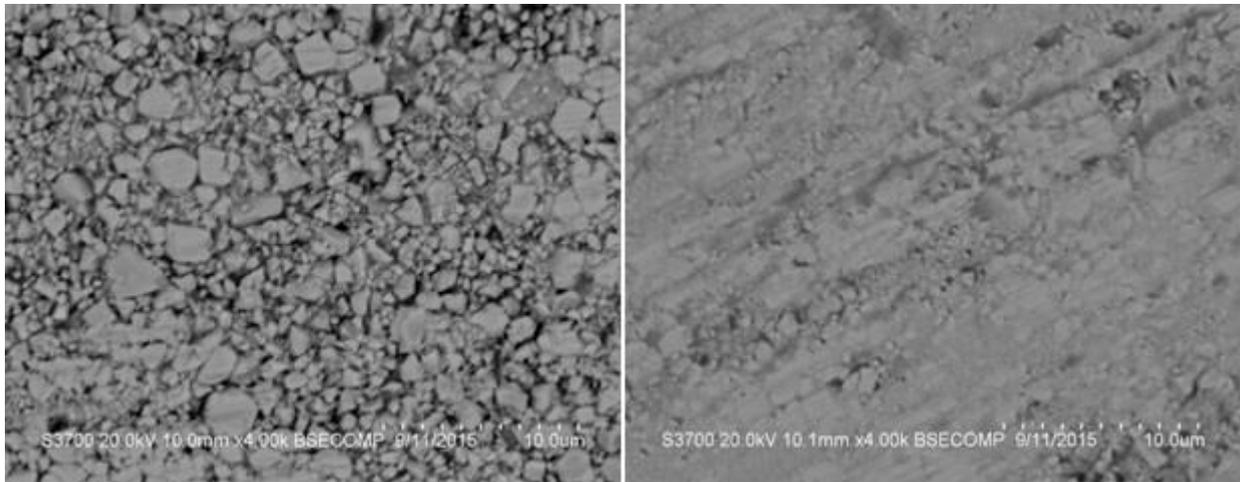


Figure 5: HVOF WC-12Co after FCA (Left) and after cathodic protection (CP) (Right)

Figure 6 shows the effect of cathodic protection on the medium carbon steel. The sliding abrasion marks are clear in both images of the UNS G10400 steel. Corrosion product and small pits were evident only on post-test surface of the carbon steel under free erosion-corrosion conditions.

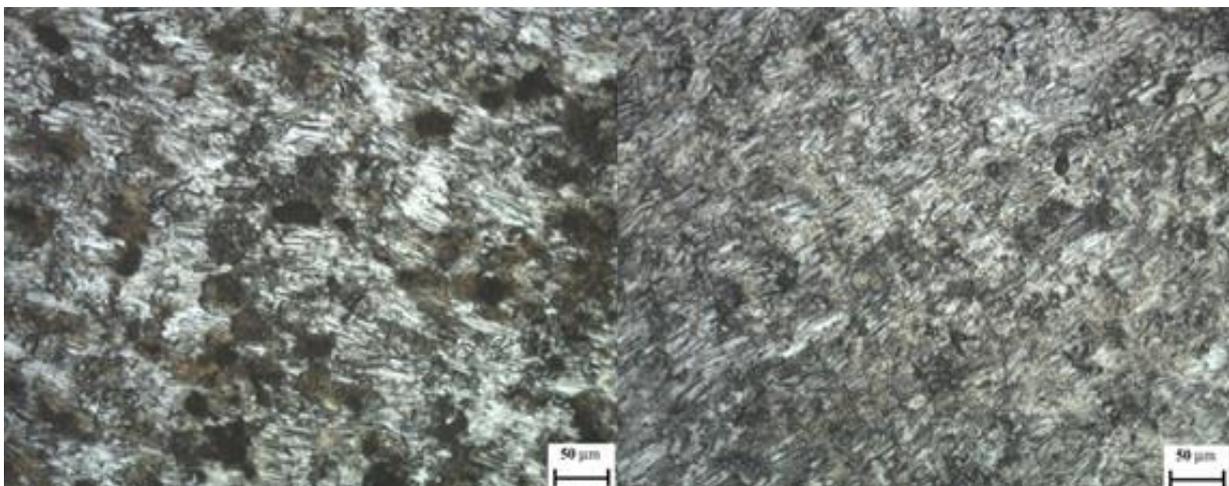


Figure 6: UNS G10400 after FCA (Left) and after CP (Right)

Figure 7 illustrates the effect of pH on the martensitic stainless steel surface. Abrasion marks are evident on the free erosion-corrosion neutral conditions with negligible corrosion product. On the other hand, the abrasion marks on the pH 3 are partially masked by copious amounts of corrosion. This is associated with the unstable passive film that cannot effectively protect the surface of the martensitic stainless steel in acidic environments.



Figure 7: UNS S42000 after FCA at pH 7 (Left) and after FCA at pH 3 (Right)

3.3 Roughness measurements

Since the roughness of the mechanical seals influences leakage, post-test roughness tests were conducted at the free corrosion abrasion (FCA) and cathodically protected coupons, as illustrated in Table 6. These were performed to investigate the effect of corrosion and synergy component on the surface topography. It should be noted that the zirconia and the DLC coating were excluded from this assessment as they were immune to any corrosion effect. According to Table 6, two groups of materials are evident; those whose surface was significantly deteriorated/roughened by corrosion and synergy processes and those for which their surface remained relatively intact. The HVOF WC-12Co coating and the medium carbon steel (UNS G10400) fall into the first group, with 62% and 41% decrease of the surface roughness, respectively, with the application of cathodic protection. On the other hand, the HVOF WC-10Ni and the martensitic stainless steel comprised the second group, by exhibiting a decrease in roughness no more than 11% with the isolation of the mechanical damage through cathodic protection.

Table 6: Post-test roughness measurements in the Outer Area

Material	Post-test surface roughness, Ra (μm)		Percentage decrease with CP (%)
	FEC	CP	
WC-12Co	0.97	0.37	62
WC-10Ni	0.44	0.42	5
UNS G10400	0.63	0.37	41
UNS S42000 pH=7	0.38	0.34	11
UNS S42000 pH=3	0.38	0.34	11

3.4 Comments on material selection

The value of understanding the operating conditions of the mechanical seals and subsequently the deterioration mechanisms that occur to optimise the material selection process is important. The material choice is also dictated by the manufacturing cost, and for this reason it has to be considered in parallel with the performance of the materials. Since repetitive impact of metal to metal surfaces, along with corrosion abrasion, is apparent on mechanical seals, Figure 8 illustrates the relationship between fracture toughness and price of the tested materials. Fracture toughness is also an important parameter to consider for mechanical seal applications which involve impacting surfaces. If the material has poor fracture toughness then the seal is most likely to fail in impact conditions.

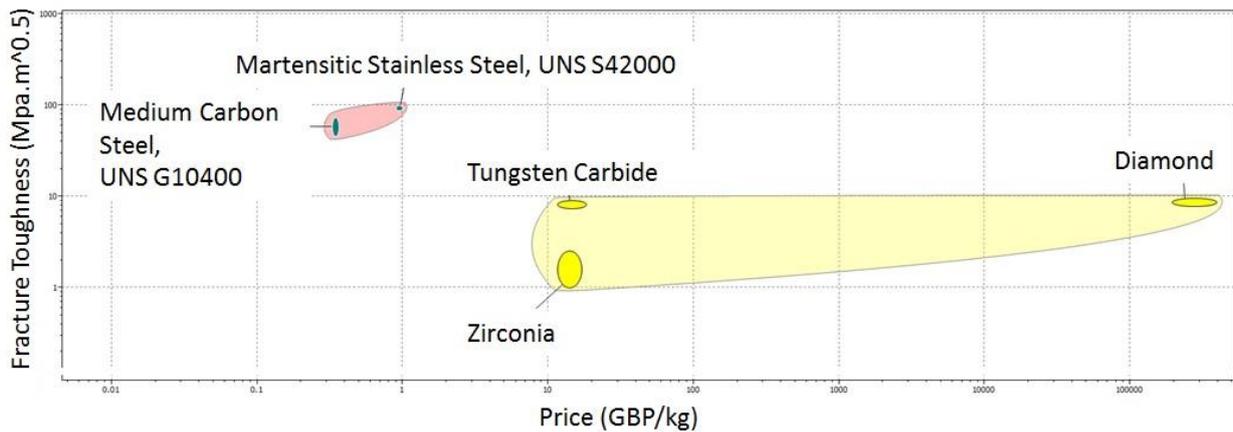


Figure 8: Fracture toughness of the studied materials versus the material's price (Cambridge Engineering Selector)

3.4.1 Ceramics

The two ceramics, Zirconia and Diamond-Like Carbon (DLC) coating, exhibited superior resistance to sliding abrasion. Studies have shown that the erodent must be 1.2 times harder than the target to cause severe fracture in abrasion events [27]. Hence, the excellent performance of the ceramics is associated with their high bulk hardness. The immunity of ceramics to corrosion provides additional advantages in engineering cases where corrosion abrasion is apparent. However, the fluid sealing engineering parts experience more than one deterioration phenomena which makes their mitigation more challenging. Corrosion-abrasion and impact is one of the most aggressive degradation events which can occur on mechanical seals (valve and seats). To counteract this type of damage, the selected material must exhibit good corrosion resistance, a great bulk hardness and relatively high fracture toughness to undertake the high impact energies. Although the Zirconia ceramic and the DLC coating exhibit great abrasion resistance, their low fracture toughness (up to $7 \text{ MPa} \cdot \text{m}^{1/2}$) make them vulnerable to cracking at high impact energies. Their low fracture toughness and their high manufacturing cost (refer to Figure 8) are the main selection drawbacks for fluid sealing applications.

3.4.2 WC based HVOF sprayed cermets

The sprayed cermet materials exhibited excellent resistance to abrasion damage due to their high hardness. It was clear, though, that the sprayed cermets were influenced by the presence of corrosion processes in the overall sliding abrasion deterioration, resulting in higher volume rates. There was a clear distinction in the overall performance of the two different sprayed cermets, with the WC-10Ni cermet performing significantly better than the WC-12Co. This feature is attributed to the rapid dissolution of the metallic binder which exposes the dense WC grains and makes them susceptible to fragmentation as they will lack mechanical support [22-25]. The Co binder is more vulnerable to corrosion than the Ni binder which explains the vast difference in performances between the two HVOF sprayed coatings [27-28]. Thus, the HVOF WC-10Ni would be preferred, as it has performed 2.5 times better than the HVOF WC-12Co in corrosion abrasion conditions. It should be mentioned that if cathodic protection can be applied in mechanical seals, both coatings would be ideal candidates. However, in corrosion abrasion with impact situations, the two HVOF sprayed coatings would have slightly better behaviour from the ceramics because of their relatively higher fracture toughness. It is evident that the effect of the binder composition is predominant to the fracture toughness of the WC-based cermets, as the increase of binder content raises the relatively low fracture toughness of the WC (maximum observed, 35GPa)[29-30]. According to Figure 8, their cost is similar to Zirconia and for this reason they are deposited onto corrosion resistant materials instead of solid sintered parts. The spray process quality should not be overlooked as coating defects, like porosity, cracks and poor adhesion, would be detrimental to their performance in all environments.

3.4.3 Medium carbon steel

The medium carbon steel exhibited the poorest corrosion abrasion resistance of all the comparative materials. Both abrasion and corrosion and synergy component damage were higher than the reference material, which indicates that the medium carbon steel would not provide any benefit in any circumstance. However, the low cost (refer to Figure 8) of the medium carbon steel enables surface hardening through diffusion processes, such as carburising, which will enhance its surface hardness and subsequently its abrasion resistance while maintaining its advantageous high toughness against impact. The surface hardening in conjunction with the application of cathodic protection would substantially improve its corrosion abrasion resistance but it is still questionable if it could exceed the performance of the other comparative materials discussed herein.

3.4.4 Martensitic stainless steel

The UNS S42000 stainless steel exhibited slightly better abrasion resistance as the reference material (UNS S31600) and the medium carbon steel as it has higher hardness, 280HV compared to 200HV (UNS S31600) and 240HV medium carbon steel. This behaviour also correlates well with the notion that brittle materials have exceptional wear resistance at low angle of attack [28]. However, the UNS S42000 martensitic stainless steels possess lower Cr and contains negligible Mo and Ni (elements which enhance corrosion resistance), hence they cannot compete with the austenitic stainless steels (>16%Cr, 12%Ni and 2.5%Mo) in terms of corrosion resistance. These compositional factors influence the martensitic stainless steel corrosion abrasion performance under neutral corrosion abrasion conditions. The impact of corrosion related component in the overall performance is more substantial in acidic environments, the martensitic stainless steel experienced substantial amounts of corrosion and synergy due to the more aggressive corrosive media, altering its good overall performance to corrosion abrasion behaviour to almost 2 times poorer than the reference material. In corrosion abrasion with impact occasions, the stainless steel

would be an adequate candidate as it combines good corrosion resistance, relatively moderate hardness and elevated fracture toughness. The cost of the stainless steel though is greater than the carbon steel (refer to Figure 8) which is an additional hindrance in selecting the former material for mechanical seals.

5. CONCLUDING REMARKS

Selection of materials for mechanical seals is complicated by the potential involvement of a number of material degradation processes, such as; mechanical abrasion, corrosion, corrosion-abrasion interactions, repetitive metal-metal impact. Cost restrictions also play an important role.

Corrosion processes generally play no part in the performance of pure ceramics (such as Zirconia and DLC coating). This feature, allied with the excellent abrasion resistance (associated with high hardness) represents an attractive combination of properties. The poor fracture toughness of pure ceramics and their high cost, however, constitutes a barrier to their application in some sealing set-ups.

Consequently, for many purposes, alternative materials have to be considered and, in relation to such materials, the role of corrosion and corrosion related processes on seal performance assumes some importance. Indeed the corrosion related component can become the dominant material degradation process. This focussed investigation has demonstrated the following:

- For the use of HVOF sprayed cermets (attractive on account of their good abrasion resistance), the choice of metal binder is crucial with, for instance, WC-Ni being much more preferable than WC-Co.
- The corrosion related damage is often profoundly influenced by the material microstructure.
- Carbon and low alloy steels experience particularly severe corrosive attack in saline environments.
- A change in fluid composition (e.g. to become acidic) can transform a material (e.g. martensitic stainless steel), with good corrosion abrasion resistance, to one of extreme vulnerability.

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