Wear Study of Metallic Interfaces for Air-Conditioning Compressors Under Submerged Lubrication in the Presence of Carbon Dioxide

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ABSTRACT

The implementation of carbon dioxide (CO₂) as an alternative refrigerant for air-conditioning compressors has gained significant attention recently. The main interest in CO₂ is related to its zero ozone depletion potential (ODP) and low global warming potential (GWP) compared to commonly used hydrofluorocarbon (HFCs) refrigerants such as R-134a. Friction and wear studies on tribological contacts commonly used in air-conditioning compressors under the presence of CO₂ are scarce in the literature. The present study focuses on the tribological behavior of Al390-T6, gray cast iron, and Mn-Si brass (UNS C67300). These materials were tested against 52100 steel shoes using a pin-on-disk configuration. The tests were performed under submerged lubrication conditions using polyalkylene glycol (PAG) lubricant in the presence of CO₂. Results showed that the wear resistance of gray cast iron and Mn-Si brass was higher compared to Al390-T6. In spite of the fact that Al390-T6 and Mn-Si brass had similar hardness, Al390-T6 showed higher wear after testing. X-Ray Fluorescence (XRF) analysis of the lubricant after testing of Al390-T6 showed the presence of eutectic silicon particles. Also, Auger Electron Spectroscopy (AES) of Al390-T6 showed an atomic concentration decreased in

silicon content after testing. Decreased in silicon content was attributed to the depletion of eutectic silicon particles, leading to a decrease in hardness and a subsequent increase in wear during the test.

KEYWORDS: Air-conditioning compressors; carbon dioxide refrigerant; Al390-T6; Mn-Si Brass; Gray cast iron; GWP; Bearing area curve; Wear; XRF; AES

1. INTRODUCTION

The concern about global warming grew in the 1990's and increased the interest of the refrigeration industries in natural refrigerants to replace HFCs (R-134a, R-407C, R-410A). Compared to HFCs (GWP of R-134 is approximately 3100), carbon dioxide (CO₂ or R744) has a negligible GWP and is inexpensive, nontoxic, and nonflammable. Also, among other natural refrigerants such as ammonia, water, air, and isobutene (R600a), CO₂ is the only one which can operate as a fluid in a vapor compression cycle at temperatures below 0 °C [1]. However, implementation of CO₂ imposes several disadvantages which include; loss of capacity, low coefficient of performance (COP) at high heat rejection temperature, and operation at very high pressures [1, 2].

Polyalkylene glycol (PAG) has been proven to be the most effective lubricant candidate for CO₂ systems for different reasons including its partial solubility with CO₂ and excellent lubrication during starved conditions compared to other synthetic lubricants such as Polyolester (POE) [2,3]. Different studies were performed on different lubricants suitable for CO₂ systems and the researchers came to the conclusion that PAG offered the best lubricity effect for transcritical applications [4]. Metallic interfaces such as Al390-T6, Mn-Si brass, and gray cast iron, are used in compressors, the first two being commonly found in swash plate type of

compressors and the last one in scroll compressors, respectively. Even though research on the tribological aspects of these materials is abundant in the literature, the behavior of these materials under the presence of CO₂ is still missing. For instance, a tribological comparison of CO₂ and R410a using synthetic lubricants such as PAG and POE under flooded lubrication conditions was performed [5]. By using Al390-T6 against 52100 steel shoes on a pin-on-disk configuration, they came to the conclusion that CO₂ performed better than R410a in terms of the wear measured on the samples after testing. They also found that a transformed layer (mainly composed of oxides and silicon) 200 nm below the sliding surface of the disk, became harder during the initial stages of the test, but weakened during the end. Cannaday and Polycarpou [6], studied the advantages of CO₂ compared to R410a using a pin-on-disk configuration. They claimed that CO₂ promoted stronger formation of oxide layers than R410a in the presence of POE under submerged lubrication conditions. In addition, an increase in the oxygen and silicon content through the testing was found when compared to the virgin state, yet there was no conclusive trend in the behavior due to the variability in the percentages of these two elements. The tribological performance of CO₂ against R134a using a pin-on-disk configuration made out of gray cast iron was studied [7]. It was not only found that CO₂ performed similarly in terms of wear and friction compared to R-134a under unlubricated conditions, but under boundary/mixed lubrication conditions using PAG lubricant. Nunez et al [8] published a direct comparison among Al390-T6, Mn-Si brass, and gray cast iron, under boundary-mixed lubrication conditions using PAG. It was found that even though Mn-Si brass has a lower mechanical strength compared to gray cast iron, they performed similarly and were superior in terms of scuffing resistance (load up to the point of failure) compared to Al390-T6. In that study the scuffing point was characterized by a sudden increase in the friction coefficient.

The objective of this work is to compare the wear performance of Al390-T6, Mn-Si brass, and gray cast iron under submerged (flooded) lubrication conditions in a CO₂ atmosphere and PAG lubricant. The tests were performed using a High Pressure Tribometer (HPT) which is a machine designed to perform tribological tests at high chamber pressures, details of the HPT can be seen in Fig. 1 [9]. The disks were tested against 52100 steel shoes using a pin-on-disk configuration. Wear type of experiments are useful for direct comparison of different environments or different materials (like in the current study). During these experiments the load is kept constant throughout the test. After testing, the variation of surface roughness with burnishing/wear was also investigated. Specifically, statistical parameters related to amplitude, as well as bearing area descriptors (such as lubricant retention indexes [2, 10] were extracted for the untested and burnished samples). Lastly, XRF was performed to analyze the PAG lubricant and Auger spectroscopy (AES) was employed to compare the change in atomic concentration of the chemical elements of the different interfaces after the experiments, respectively.

2. EXPERIMENTAL PROCEDURE

2.1 Controlled tribological experiments

Using a pin-on-disk configuration, one set of experiments was designed and performed. During this set, the load was kept constant throughout the tests in order to study the wear performance of the different tribopairs. PAG lubricant (Idemitsu Kosan Co., Ltd. PZ 68ZL) was used (chemical composition of PAG can be found on [11]). This lubricant was specifically manufactured for use with CO₂ as a refrigerant. A constant normal load of 1340 N was used for 20 minutes and the interface was submerged in a pool of PAG lubricant. The CO₂ pressure was kept constant at 1.4 MPa, the temperature at 90 °C, while the rotational speed was set constant at 1000 rpm (which corresponds to a linear speed of 2.4 m/s). The normal load and the duration of the tests were selected in such a way that under the conditions of submerged lubrication and contact geometry wear was caused on the surface of the disks. The chamber pressure was maintained at 1.4 MPa (~200 psi) to avoid damage of the sealing of the tribometer. The chamber temperature of 90 °C was selected to simulate the behavior of compressors under idle conditions. Before initiating a test, the samples were immersed in a pool of acetone and ultrasonically cleaned, then rinsed with alcohol and dried using warm air. In order to ensure repeatability each experiment was performed twice. In the contact geometry used for these experiments, the pin (shoe) was the lower stationary part, while the disk was the upper rotating part (see Fig. 1). Typical samples and shoes used during the experiments are shown in Fig.2 (a) through Fig. 2 (d), respectively. It should be noted that the area of the shoe was reduced from 12 mm (original diameter) to 6.35 mm to increase the contact pressure at the interface (increasing the wear), the shoe also has a dimple (which helps to retain lubricant) and is crowned [12].

In order to ensure similar surface roughness, all disks were machined and polished using the lapping technique. Lapping was performed placing a normal load on the disks used during the experiments, and then rubbing its surface against a rotational lapping disk. Both surfaces slid in the middle of a slurry film composed of aluminum oxide particles. These particles abrade the surface of the disk and provide the final finishing. The root-mean square roughness (R_q) of the samples was determined using 10 mm-long profilometric scans for the disks and was approximately $0.7\text{ }\mu\text{m}$, while for the SAE 52100 steel shoes, 1 mm-long profilometric scans were employed and the surface roughness R_q was approximately 50 nm.

2.2 Surface roughness measurements

Surface roughness changes when surfaces in contact experience wear during tribological testing. Changes in surface roughness can vary depending on the stage of testing from running-in, to mild burnishing, to deep wear produced as a result of scuffing. Root-mean square and center-line average are the most commonly used amplitude descriptors to characterize surface roughness with line scans. However, these parameters do not provide enough information about the variation of surface roughness because the contact at the interface is represented by an area and line scans do not take into account features across an area. Instead, Birmingham-14 parameters can be used to quantify geometrical and functional properties of the surface [13]. In this study, 2D areal scans were performed using a contact profilometer on the samples. A Tencor P-15 3-D profilometer was used and scans were performed over an area of $500\text{ }\mu\text{m}$ by $500\text{ }\mu\text{m}$ in two different locations for each disk of the three different materials. Specifically, scans were performed on a virgin or untested region (outside the wear track) and inside the wear track (tested region).

Analysis of the data obtained from the 2D surface roughness scans, allows the calculation of statistical parameters based on the bearing area curve (Abbott-Firestone curve). From these statistical parameters, the topographical changes and fluid retention capacity of the surface were selected as the most important descriptors as the surfaces undergo burnishing/wear. A bearing area curve can be described by three regions when lines at 5% and 80% of the bearing area ratio are drawn. These regions are, the material volume in the peak zone (S_m) (0-5%), the void volume in the core zone (S_c) (5-80%), and the void volume in the valley zone (S_v) (80-100%) respectively [2]. A detail explanation and the expressions that describe these three functional coefficients can be found in Suh et al [10] and ASME [14].

2.3 SEM

A JSM-6060LV was used to study the microstructure of the different alloys before testing. The instrument uses a high accelerating voltage of 0.5-30 kV and a probe current of 1 pA to ~1000 nA. Secondary electron (SE) image and backscattered electron (BSE) image modes are available for purposes of topography and composition analysis.

2.4. AES

Auger Electron Spectroscopy (AES) was performed in a physical electronics model PHI 660 Scanning Auger Microprobe (SAM) which has capability of elemental mapping with high spatial resolution. This equipment has a coaxial LaB6 filament electron gun of approximately 100 nm minimum spot size for Auger analysis and accelerating voltage of 0.5 to 20 kV. Measurements were performed inside the wear track of the disks tested in order to quantify changes in atomic concentration of different elements in the three different materials to provide

answers about the wear mechanisms. During measurements, a sputter rate of 10 nm/min was used to convert the collected data into sputter depth (nm). This rate was constant through the AES measurements. Sputter duration was chosen to provide a depth of approximately 200 nm below the surface for the three samples. Different locations were chosen for the measurements inside and outside the wear track, leading to similar results. Therefore, only one measurement was chosen as representative for the results and discussion.

2.5. XRF

XRF experiments were performed in a Kevex analyst chamber/spectrometer with an X-ray tube as primary excitation mode. The target current varied from 0-3.3 mA and the voltage from 0-60 kV. XRF was performed by analysis of a sample of the liquid lubricant (a few ml of the lubricant were placed inside a container) before and after the tests, with the objective to investigate its chemical changes. This technique is useful to study the chemical composition of lubricants since it uses a low vacuum pressure during the analysis. During this analysis, Ti and Rh were used as primary excitation elements to obtain the spectrum.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Microstructural study of virgin samples

3.1.1. Aluminum 390-T6

Al390-T6 is a hypereutectic soft aluminum based matrix alloy, reinforced with hard silicon particles. The purpose of adding silicon particles in this alloy is to improve its wear resistance. The chemical composition of Al390-T6, shows that silicon has a percentage of 16 to 18%, which is dispersed throughout the Al matrix to enhance its wear resistance, as seen in Table

1 [8]. As observed in Fig.3(a) from an SEM image at 1800X, the morphology of silicon particles in the matrix is non-uniform, Al390-T6 is composed of primary silicon particles and eutectic silicon particles (which have a more uniform distribution in the matrix), the primary silicon particles being responsible for the improvement of strength and wear resistance of this alloy [15, 16].

3.1.2. Gray Cast Iron

Gray cast irons in commercial alloys have a percentage of carbon from 2.14 to 4.5% and are mainly formed by addition of silicon. In gray cast iron, the amount of carbon that surpass solubility in the austenite precipitates and form graphite flakes, formation of graphite is not only regulated by silicon, but from slower cooling rates in the solidification. Table 1 shows the chemical composition of gray cast iron, while Fig. 3(b) shows the sharp edges of the graphite flakes which are surrounded by a pearlitic structure (As seen in Table 1 a content of Mn from 0.7-0.8% corresponds to pearlitic gray cast iron) .

3.1.3. Manganese-silicon brass

Mn-Si brass is an alloy commonly found in applications where high tensile strength, good wear resistance, low friction coefficient, and low weight are desirable. The microstructure of Mn-Si brass (UNS C67300) consists of a copper rich α soft phase matrix, a combined (copper-zinc) β' phase, and a manganese silicide phase (Mn_5Si_3) which enhances its mechanical strength. Chemical composition of manganese silicon brass is shown in Table 1, while Fig. 3(c) shows its microstructure [8]. Pugacheva [17] reported that manganese and silicon present in the form of Mn_5Si_3 improves the fatigue resistance of Mn-Si-Brass by increasing its tensile strength, as well as its corrosive resistance and ductility. Turhan et al [18], showed that lead is responsible for the

hot brittleness in copper alloys when its content exceeds 0.5% being segregated along the grain boundaries, but provides free machining characteristics to this alloy due to its lubricity properties. For instance, Nunez et al [8] proved that scuffing of Mn-Si-brass was not as severe as in Al-390T6 and gray cast iron. They showed through SEM-EDS that lead retarded the onset of scuffing by providing further lubricity effect.

3.2 Controlled tribological wear experiments

Experimental results are shown from Fig. 4(a) through Fig. 4(c). Fig. 4(a) shows the friction coefficient for the Al390-T6 sample, which started at approximately 0.1 and reached a steady state value of approximately 0.03. The peak at about 10 minutes in the friction coefficient during Test 1 in Fig. 4(a) might be caused by the wear debris particles generated during the testing which due to the high normal load caused an abrupt increase in friction force. In the case of the gray cast iron sample the friction coefficient started at approximately 0.1 and reached a steady state of approximately 0.08 as seen in Fig. 4 (b). For the case of the Mn-Si brass sample friction coefficient also started at approximately 0.1 and reached a steady value of approximately 0.05 (Fig. 4(c)).

Single line profilometric scans were performed after the tests for every material as seen in Fig. 5. Fig. 5(a) shows typical wear scan for the Al390-T6 sample which showed the highest wear ($\sim 0.6 \mu\text{m}$) compared to the case of gray cast iron (Fig. 5(b)), and Mn-Si brass samples (Fig. 5(c)), where the wear depth was approximately $0.1 \mu\text{m}$ and $0.3 \mu\text{m}$, respectively. These results can be explained if we consider the hardness of the three materials (measurements were performed using micro Vickers hardness testing). Al390-T6 was the softest material with a hardness of 1.3 GPa, followed by Mn-Si brass (1.4 GPa), and the gray cast iron (2.3 GPa) .

Despite the fact that Mn-Si brass and Al390-T6 showed similar hardness values, the wear of Al390-T6 was higher. This behavior can be explained based on the high percentage of silicon (16-18%) in hypereutectic Al390-T6. As will be explained in a later section of this paper through AES and XRF, during submerged lubrication some of the eutectic silicon particles (small particles) present in the Al390-T6 at the surface roughness level (a few microns below the surface) are being pulled out of the matrix. The small eutectic silicon particles are harder (~10 GPa using Vickers hardness testing [19]) than the 52100 steel shoe (~8.3 GPa using Vickers hardness); therefore, once they are pulled out of the aluminum matrix, they act as abrasive third bodies. As a consequence, Al390-T6 weakens at the surface roughness level which results in higher wear compared to Mn-Si brass.

3.3 Surface topographical measurements

2D scans were performed on the three different samples before and after testing. Changes in the topography of the surface were observed, as can be seen when Fig 6 (a) is compared with Fig. 6 (b). Since the wear was not significant (less than 1 μm) and there was only mild-burnishing of the asperities during the constant load experiments (Fig. 5), Birmingham-14 parameters were calculated with a focus on fluid retention parameters. Functional retention parameters showed clear differences between the three different surfaces tested. From these data, root-mean square (S_q) and skewness (S_{sk}) values were extracted and summarized in Table 2. After testing, the value of R_q of the Al390-T6 disk decreased by 58% while the reduction of R_q for the gray cast iron and Mn-Si brass was 16 and 30% respectively. Moreover, skewness which is considered a measure of the deviation from Gaussian distribution has been reported to be negative for engineering samples (Cavatorta and Cusano [9]). After testing, skewness

decreased by 80% for Al390-T6, while a decrease in 3 and 30% was found in gray cast iron and Mn-Si brass, respectively. Larger changes of R_q and S_{sk} values in the case Al390-T6 indicate a higher degree of burnishing, compare to gray cast iron and Mn-Si brass.

In addition, functional volume parameters provide information related to the material and fluid retention properties of the surfaces. These parameters were also extracted to evaluate the functional performance of the three surfaces. From these parameters, the core void volume is defined between 10% and 80% of the bearing area curve and is the “empty” volume contained when 10% to 80% of the asperities are in contact [20]. As seen in Table 2, after testing, the core void volume of the surface (S_c) decreased by 69% for the Al390-T6 disk and approximately in 30% and 41% for gray cast iron and Mn-Si brass respectively. Also, the material volume of the surface (a measure of the material of the asperities at 100% of the bearing area curve) for the Al390-T6 disk decreased by 52.5% compared to gray cast iron and Mn-Si brass where this parameter reduced in approximately 20 and 31% respectively. The reduction of material volume can be explained by a decrease in mass and volume as the asperities get burnished. Moreover, the valley void volume of the surface (defined between 80-100% of the bearing area curve) decreased by 52% for Al390-T6 and approximately 21% and 35% for gray cast iron and Mn-Si brass, respectively. Clearly, these results prove that Al390-T6 experiences more burnishing compared to gray cast iron and Mn-Si brass.

3.4. AES Results

As can be seen in Fig 7 (a) the atomic concentration of oxygen outside of the wear track in Al390-T6 is higher in the first 10 nm below the surface and then it starts decreasing with sputter depth. This is due to the presence of a very thin oxide layer caused by oxidation of the

sample. The same tendency was observed inside the wear track (Fig. 7 (b)), probably due to oxidation of the sample and exposure to the ambient air between analyses. Also, an increase in approximately 17% in carbon was observed comparing the atomic compositions outside and inside wear track. Interestingly, a decrease of 8% and 12% was observed for Si and Al respectively, when comparing outside and inside wear track compositions. This suggests that indeed Al390-T6 lost silicon particles during the constant load experiments, losing its main strengthening component.

In the case of gray cast iron and Mn-Si brass, the atomic concentration of oxygen and carbon was unsteady in the first 10 nm compared to Al390-T6. As seen in Fig. 8 and Fig. 9 oxygen and carbon showed higher values up to the first 10 nm and then the atomic concentration became approximately steady. However, in the case of gray cast iron an increase in the atomic percentage of carbon (22%) was observed after the experiments. It is believed that this increase is due to the exposure of graphite flakes after testing. In addition, both materials showed a decrease in the percentage of silicon. Silicon decreased in 4% and 13% for gray cast iron and Mn-Si brass respectively. In the case of manganese a reduction in 25% was observed for gray cast iron and Mn-Si brass, respectively. A reduction in silicon is responsible for a decrease in strength and wear resistance of gray cast iron and Mn-Si brass, while a reduction in manganese affects the strength and the fatigue resistance of Mn-Si brass [18]. Note that the atomic percentage of Cu is steady inside the wear track in Fig 9 (b) (a zoom-in was added to better observe the trends in the atomic concentration). It is believed that preferential loss of Si and Mn during wear testing of Mn-Si brass left a Cu rich α phase being the reason why a higher percentage of Cu is observed after testing (inside wear track, Fig 9 (b)) compared to an untested virgin region (Fig 9 (a))

3.5. XRF studies of the PAG lubricant

Based on visual inspection of the PAG lubricant after testing of the Al-390T6 sample, it was noticed that the lubricant turned dark in appearance. That was not the case after testing of gray cast iron and Mn-Si brass. Based on the XRF analysis (plot is not shown) of the lubricant before and after testing, it was noticed the presence of Si, which is attributed to the loss of eutectic silicon particles and is what explains the change in color of the lubricant and the weakening of Al390-T6 at the asperity level during the wear tests (it should be noticed that wear in Al-390T6 was only $\sim 0.6 \mu\text{m}$ which is similar to the initial surface roughness of the sample). Presence of other elements such as Ca, and K was noticed and can be attributed to contamination, while P it is believed to be related to the additives present in the chemical structure of PAG. Traces of other elements such as Al and Fe can be related to the chemical structure of Al390-T6.

CONCLUSIONS

Profilometric measurements and 2D surface roughness analysis through the wear tracks generated during wear experiments for the three different materials showed that gray cast iron had the lowest wear and highest material and fluid retention capacity compared to the other two materials and this was in agreement with hardness measurements. Through XRF, it was confirmed that preferential loss of eutectic silicon particles was responsible for the decrease in strength and hardness in Al390-T6 during the experiments. By using AES it was also confirmed a decrease in the atomic silicon content of Al390-T6 when comparing spots outside and inside the wear tracks, which further suggests the loss of silicon content in this material during testing. Experimental results using the two previously mentioned characterization techniques proved that

even though Al390-T6 and Mn-Si brass had similar initial hardness, Al390-T6 lost hardness and structural strength during the experiment (due to loss of silicon), leading to higher wear after testing.

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Fig. 9— AES depth profiling data of elemental atomic concentration in Mn-Si brass, (a) outside wear track (b) and inside wear track

TABLES

Table 1— Chemical composition of Al-390T6, Gray cast iron, and Mn-Si brass

Elements	Specified chemical percentage weight (wt%)		
	Al-390T6	Gray cast iron	Mn-Si brass
Al	76	-	0.01
C	-	3.20-3.70	-
Cu	3.00-4.00	-	60.40
Fe	1.00	Balanced	0.23
Mg	0.40-1.00	-	-
Mn	0.50	0.70-0.80	2.43
Pb	-	-	1.24
Si	16-18.5	2.20-2.55	0.86
Zn	1.00	-	35.58

Table 2— Surface Roughness Parameters for the Samples Tested during Wear Experiments

Parameter	Al390-T6		Gray cast iron		Mn-Si brass	
	Virgin Region	Wear Track	Virgin Region	Wear Track	Virgin Region	Wear Track
S_q (μm)	776.61	324.05	652.63	547.82	734.61	510.20
S_{sk}	-1.76	-3.16	-1.35	-1.39	-0.30	-0.39
S_c (nm^3/nm^2)	668.22	207.43	723.49	504.79	869.90	509.38
S_m (nm^3/nm^2)	22.77	10.81	18.24	14.64	25.11	17.27
S_v (nm^3/nm^2)	140.86	66.81	118.31	93.50	89.28	57.55

FIGURES

Fig. 1—Details of the High Pressure Tribometer (HPT); a) schematic of the equipment; b) sliding interface; c) details of the shoe holder

Fig. 2—Samples used for testing; (a) Al390-T6, (b) Gray cast iron, (c) Mn-Si brass, (d) SAE 52100 Steel pin

Fig. 3—SEM microscopy images of the cross section of the different sample disks; (a) Al-390T6, (b) gray cast iron, (c) Mn-Si brass

Fig. 4— Submerged experiments for (a); Al390-T6, (b); gray cast iron, and (c); Mn-Si brass at 90 °C. Normal load was set at 1340 N.

Fig. 5— Profilometric line scans of the samples tested under submerged experiments for (a) Al390-T6, (b) gray cast iron, and (c) Mn-Si brass.

Fig. 6— Typical 2D roughness measurements of the samples; (a) before testing, (b) after testing.

Fig. 7— AES depth profiling data of elemental atomic concentration in Al390-T6, (a) outside wear track (b) and inside wear track

Fig. 8— AES depth profiling data of elemental atomic concentration in gray cast iron, (a) outside wear track (b) and inside wear track

Fig. 9— AES depth profiling data of elemental atomic concentration in Mn-Si brass, (a) outside wear track (b) and inside wear track