Friction and Wear Study of Fe-Cu-C-CaF₂ Self-lubricating Composite at High Speed and High Temperature

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Abstract. A novel Fe-Cu-C based self-lubricating composite is developed, wherein Calcium fluoride (CaF₂) has been used as a solid lubricant. CaF₂ is added in varying weight percentages of 3, 6, 9 and 12% to the base matrix comprising of Iron, Copper and Graphite (Fe-2Cu-0.8C). The composites were fabricated through Powder Metallurgy using uni-axial compaction and sintering. The developed composites were tested for friction and wear characteristics using a pin-on-disc configuration, conducted at a speed and load of 10 m/s and 20 N respectively. All tests were conducted at high temperature of 500°C for a constant sliding distance of 4000 m. Results show low coefficient of friction for the composites with 3-9 wt% CaF₂ making them self-lubricating. Due to testing at high temperature, weight gain was observed in all the composites because of oxidation. The increase in weight gain was observed to be dependent on the CaF₂ content. Adhesion, ploughing and delamination were identified to be the prominent wear mechanisms of the developed self-lubricating composites as revealed by SEM analysis.

1. Introduction
The continuous use of sliding/moving parts relative to each other in various industries, household appliances, automotive sectors etc., has led to developments in the area of self-lubricating materials. Self-lubricating materials comprises of either one or more number of solid lubricants as reinforcement incorporated in the base matrix consisting of a metal, polymer ceramic, etc. Solid lubricants such as h-BN, graphite, molybdenum disulfide (MoS₂), etc. are being widely used in these matrices [1-5]. The lubricating behavior of solid lubricants also depends upon working environment, e.g., graphite is more effective in moist conditions whereas dry conditions are more suitable for MoS₂. Researchers have also tried Boron Nitride (BN), Calcium Fluoride (CaF₂), Antimony (Sb), Tin, (Sn) and Silver (Ag), Tungsten disulphide (WS₂) as solid lubricants [6-10] with different base matrices. Also, fluorides of calcium, barium etc. have shown high thermal and oxidation resistance when compared to other solid lubricants [11-12]. It has been observed that there is an increase in the lubrication capability of fluorides at higher temperatures. This is due to the transition from brittle to ductile phases of fluorides causing low shear strength, thus resulting in lubrication [13]. Iron, being economical amongst other metals is used as base matrix in numerous applications. Copper, nickel, graphite etc. are alloyed in iron to obtain enhanced mechanical properties. The addition of antimony as a reinforcement in iron matrix has shown increase in hardness and compressive strength of the composites [14]. The tribological behavior of various steels...
was enhanced by using solid lubricants as additives such as h-BN and MoS\textsubscript{2}[15,16]. Fluorides such as CaF\textsubscript{2} and BaF\textsubscript{2} when tried with sintered Fe based composites have resulted in low friction and wear [17-19]. The wear loss of high speed steels is found to decrease on adding TiC, whereas the addition of CaF\textsubscript{2} and MnS to steels led to increased lubrication properties [20]. Fe has been associated with many base matrices, and Fe-Cu-C is the one which is being widely used in different applications due to its properties such as high hardness, strength, etc. However, Fe-Cu-C alloys are not very effective tribological candidates and hence solid lubricant additives are incorporated with the view of enhancing their tribological characteristics. Various metals and lubricants have been tried with Fe-Cu-C in order to improve both, tribological and mechanical properties [15,21-22]. Along with different reinforcement materials, the operating parameters also play an important role, e.g., working temperature, speeds, load etc, in influencing the wear and friction properties [23-26].

In the present work, Fe-Cu-C composites are investigated for their tribological behavior at high speed and high temperature. The Fe-Cu-C base matrix has been reinforced with CaF\textsubscript{2} solid lubricant in different weight percentages. Tribological tests were carried out at speed and load of 10 m/s and 20 N respectively, at the high temperature of 500°C. The wear mechanism and the surface morphology were investigated using optical microscope and scanning electron microscope (SEM).

2. Materials and Methods

Powder Metallurgy technique comprising of uni-axial compaction and sintering has been used to prepare samples from the compositions as shown in Table 1. In order to obtain a homogeneous blend of powders, the mixing was done in two steps: (i) the powders of Fe, Cu, C and CaF\textsubscript{2} were initially blended in a mortar pestle for a duration of 15 minutes and (ii) followed by mixing in a double cone mixer for 30 minutes at a speed of 100 rpm. The lubrication between the compact and the die walls, and also within the powder particles has been ensured by mixing zinc stearate to the powders of various compositions. The average particle size of Fe, Cu, C and CaF\textsubscript{2} powders were around 75 μm, 50 μm, 50 μm and 10 μm respectively. The powder after mixing were compacted in a cylindrical die at a pressure of 600 MPa. The green compacts were then obtained in the form of cylindrical pins and were sintered at 1120 °C in an inert atmosphere consisting of 90 % nitrogen and 10 % hydrogen for 30 minutes.

| Material | Compositions (wt%) |
|----------|-------------------|
| Elements | Fe   | Cu  | C   | CaF\textsubscript{2} |
| Sample 1 | 97.2 | 2   | 0.8 | 0          |
| Sample 2 | 94.2 | 2   | 0.8 | 3          |
| Sample 3 | 91.2 | 2   | 0.8 | 6          |
| Sample 4 | 88.2 | 2   | 0.8 | 9          |
| Sample 5 | 85.2 | 2   | 0.8 | 12         |

The density of the prepared composite samples was determined using Archimedes principle and hardness was measured using Vickers hardness tester. Hardness testing was carried out at a load of 50 N, and for each test sample, an average of 5 measurements was taken. The tribological testing was carried out using a Pin on Disc (POD) tribometer. En 31 steel disc having hardness of 60±2HRC was used as the counterface material for wear and friction testing. Cylindrical samples of 8 mm diameter were used for friction and wear tests. Prior to friction and wear tests, each sample was polished with 800 and 1000 grade emery papers followed by cleaning of the samples with acetone. The weight of each cleaned sample was recorded. Tribological testing was carried out at a constant load of 20 N and speed of 10 m/s at high temperature of 500 °C. During friction and wear testing, sliding distance was maintained at 4000 m. Each test was repeated for three times, and average value is reported. The wear gain or loss tabulated was determined from the change in the weight of the sample prior to and after the
tests under similar test conditions. Frictional force was obtained directly from the machine. Optical and scanning electron microscopy were used to study the surface morphology and wear mechanisms. The images of the worn samples were analysed using a JEOL JSM 5600 LV scanning electron microscope.

3. Results and Discussions

3.1. Optical Microscopy
The optical microscopy carried out on the samples revealed grain refinement in the CaF$_2$ added samples. The difference in the grain refinement is shown in Fig.1, where grain refinement in sample with 3 wt% CaF$_2$ (Fig.1 (b)) is clearly observed as compared to the base matrix (Fig.1 (a)).

![Optical images of a) Sample 1 (Base matrix) b) Sample 2 (with 3 wt.% CaF$_2$)](image)

Fig. 1. Optical images of a) Sample 1 (Base matrix) b) Sample 2 (with 3 wt.% CaF$_2$)

3.2. Density, Hardness and Porosity
Fig. 2 shows the density of the composites determined using Archimedes’principle. There is a slight decrease in the density of the sample with 3 wt% CaF$_2$ as compared to the sample with 0 wt% CaF$_2$ i.e., base matrix. The samples with weight percentage of 6, 9 and 12 CaF$_2$ has shown further decrease in density. This decrease is density is mainly attributed to the addition of low density CaF$_2$ to the base matrix.

Fig 3 shows the variation of hardness with increasing CaF$_2$ addition. A decreasing trend is observed in the hardness values of the samples, except for sample 2 as shown in Fig.3. Sample 2 that has 3% CaF$_2$ shows higher hardness due to grain refinement as depicted in Fig.1 because of the addition of CaF$_2$ reinforcement [18, 27]. The decreasing trend in the hardness of rest of the samples is attributed to the increasing porosity as shown in Fig.4. The addition of fluoride resulting in increased porosity has been reported earlier [28].

![Density of Fe-Cu-C matrix and Fe-Cu-C-CaF2 composites](image)

Fig.2. Density of Fe-Cu-C matrix and Fe-Cu-C-CaF2 composites

![Hardness of Fe-Cu-C matrix and Fe-Cu-C-CaF2 composites](image)

Fig.3. Hardness of Fe-Cu-C matrix and Fe-Cu-C-CaF2 composites
3.3 Tribological testing at High Speed and High Load

Fig. 5 shows the coefficient of friction of the test samples tested at 550 °C. From the figure, it could be seen that at the tested high speed (10 m/s) and high load (20 N) conditions waviness is observed in the friction curves as shown in Fig. 5. The waviness or fluctuation in the curves is observed to increase initially, and this is attributed to the frequent formation and removal of oxides. However, stability in the curves is observed after sliding through a distance of 1500 m. Fig. 6 shows the variation in the average values of frictional coefficient of all the samples. Initially, a decreasing trend is observed from base matrix to sample with 6 wt % CaF$_2$, followed by an increase up to sample with 12 wt % CaF$_2$. The decrease in COF from base matrix to sample with 6 wt % CaF$_2$ is due to the dominant effect of solid lubricant over hard iron oxides. Upto 6 wt % CaF$_2$, dominance of solid lubricant was observed, and thus decrease in friction values is seen. The hard iron oxides are abrasive in nature and they tend to increase the friction, which is the case in the samples with > 6 wt.% CaF$_2$. SEM images show less ploughing for 3% CaF$_2$ (shown in Fig. 8(a)) as compared to Fig. 8(b) and Fig 8(c) for samples with higher CaF$_2$ contents. Increased ploughing is ascribed to the increased formation of hard iron oxides. The increase in the presence of oxides is due to the increased porosity, thus indicating the dominant effect of hard oxides over the solid lubricant from 6 wt % to 12 wt % CaF$_2$ added samples. The average value of COF lies between 0.331-0.352.

Also due to high temperature, weight gain resulted during wear as shown in Fig. 7. It is observed that except for the base matrix, all CaF$_2$ added samples exhibited increased weight gain, which is primarily due to the compacted and sintered glaze layers formed on the worn surfaces. The upward slope indicates weight loss which is due to the oxide formation, i.e., oxide formation in sample with 3wt% CaF$_2$ is less when compared with rest of the samples. The increase in weight gain from 3 wt % to 12 wt % CaF$_2$ added samples is mainly due to the increased oxidation resulting from increased porosity. Despite weight gain, the samples with weight percentage of 9 and 12 CaF$_2$ shows more wear than oxidation, which may be attributed to their initial low hardness values.
4. Conclusions

In this paper, Fe-Cu-C based self-lubricating composites have been developed wherein CaF$_2$ as a solid lubricant was reinforced to the base matrix using single-stage compaction and sintering process. The
developed composites were investigated for density, porosity, hardness, friction and wear. The following are the conclusions drawn:

- The density of fabricated composites decreases with the increase in CaF₂ content and the porosity increased with the addition of CaF₂.
- The hardness of the composites also decreased with the increase in CaF₂ addition except for the composite with 3 wt% CaF₂. This is due to the grain refinement due to addition of small amount of CaF₂.
- The friction coefficient of the developed composites with CaF₂ up to 6 wt% is less as compared to rest of the composites which is due to the role of solid lubricant and hard iron oxides.
- Weight gain resulted in the composites due to oxidation. However, weight gain of CaF₂ added composites is more than that of the base matrix.
- Based upon the above stated facts, it is evident that the developed composites can be used in antifriction applications at high temperature and high speed.

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