



Corrosion of Cast Iron Mill Plates in Wet Grinding

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Abstract

Corrosion studies were carried out on two different maize grinding plates. Maize was soaked in water for three days and the water decanted and used as electrolyte. Mass loss and pH measurements were carried out every 3 days for 15-day period. Results show that, for each plate, mass loss and pH increased with exposure time. Corrosion rates determined from mass loss data was found to be strongly dependent on pH. The observed behaviour may be explained in terms of the chemical composition and/or microstructures of the plates. Results are briefly discussed in terms of the contribution of corrosion to wear.

Keywords

Iron; Weight loss; Rust; Selective oxidation; Wear

Introduction

A large amount of unforeseen incidents that occur in food processing and distribution channels such as possible toxic effects, are related to corrosion and erosion [1]. Removal of metal from the surfaces of grinding plates occurs in both dry and wet grinding. The factors

affecting wear are governed by the distribution and characteristics of micro constituents in the metal or alloy. Additional corrosive-wear is apparent during wet grinding in which less resistant corrosion product films are abraded away, contaminating the processed food. The degree of contamination depends on pH of the environment, chemical composition, microstructure, and hardness of the mill plate materials. Corrosion management is therefore essential to maintain the integrity of the facility. The metallurgy of food processing equipments such as corn-mill machine usually uses cast iron plates because of its good mechanical properties and is also relatively cost effective. Nevertheless, cast iron is strongly susceptible to corrosion attack in food product environments due to their acidic nature. A quantitative understanding of the corrosion rate of cast iron plates under wet grinding would be a key factor in providing an accurate risk assessment of the attack of the equipment part made from these materials.

Earlier research carried out on the wearability of corn-mill grinding plates has shown that the corn-mill plates that are used in wet grinding tend to wear faster than corn-mill plates used in dry grinding [2]. Moisture plays an active role in the corrosion of iron. Usually, the corrosion product is not adherent and therefore corrosion continues unabated resulting in material degradation. The synergistic attack of corrosion and wear of corn-mill grinding plates has not been investigated, even though it results in serious damage to wear/corrosion resistant materials. In a related work, it has been found that corrosion plays significant role in wearability of cast iron ball-mill grinding media during wet grinding. The contribution was estimated to be in the range of 10-90% [3]. It has therefore become necessary to investigate the effect of corrosion on the wearability of cast iron corn-mill grinding plates. Better understanding of the early degradation of cast-iron mill plates could go a long way to enhance the mechanical properties and hence reduce iron contamination in milled maize. Iron contamination in milled maize could result in dietary iron overload when consumed. Some of the major health hazards are liver infections and anaemia [4, 5].

In this work, corrosion behaviours of two different cast iron corn-mill plates have been investigated using mass loss measurements. The relationship between pH and corrosion rate has been developed and subsequently linked to its effect on the wearability of corn-mill plates when used in wet grinding environments. Relationship between microstructure and corrosion rates in the cast iron materials was also determined.



Materials and Methods

Corrosion experiments were performed using two corn-mill plates, herein referred to as CAL and NUL. The chemical compositions of the two mill-plates were determined using mass spectrometer (Angstrom V 960). Microstructures were analyzed using Lecia DM 1000 optical microscope attached to a camera. Before carrying out microstructural studies, specimens were polished on an Emery cloth using alumina (0.5 μm) as a lubricant. The volume fractions of the phases were measured quantitatively using Image Tool[®] (version 3.0). Total immersion corrosion tests were carried out in accordance with ASTM standard G31-72 [6]. Test specimens were prepared by grinding off the burrs on both sides of the plate to obtain a somewhat smooth surface. The plates were then ground and cut into rectangular shapes having dimensions of 50 mm \times 25 mm \times 10 mm. The specimens were then abraded through successive grades of silicon carbide papers to 1000 grit. Before immersion, the specimens were ultrasonically cleaned in alcohol to remove any dirt on the surface. The specimens were then weighed to an accuracy of 0.0001g before immersing in the corrosive medium. A separate test cell was used for each specimen. Test involved immersing simultaneously two specimens in at least 3 litres of the electrolyte. Maize (corn) was steeped in water for three days and the water decanted and used as the electrolyte. This electrolyte was chosen to simulate the service condition where maize is soaked in water for three to four days to soften it before milling for certain delicacies [7]. The pH of the solution was measured before and after immersion of specimens. At the end of the immersion period, specimens were cleaned by abrading on 120 grades silicon carbide abrasive paper in accordance with ASTM standard [6]. Mass loss was determined after every cleaning cycle and average mass loss (of the two specimens) versus exposure time was plotted. All tests were carried out at room temperature (30°C). The average corrosion rates (ACR) were calculated from the mass loss measurements using the following formula:

$$\text{ACR} = M/At \quad (1)$$

where M is the mass loss (mg), A is the exposed surface area (cm^2), and t is the exposure time (days).

Results and Discussion

Chemical Composition and Microstructure of Mill-Plates

The chemical compositions of the two corn-mill plates are shown in Table 1.

Table 1. Chemical composition (wt.%) of corn-mill plates specimens

Composition	C	Mn	P	S	Si	Cu	Ni	Cr	Mo	Fe	CE	Mn:S Ratio
CAL	3.37	0.64	0.13	0.12	0.72	0.03	0.52	1.18	0.23	Matrix	3.65	5.33
NUL	3.12	0.29	0.28	0.04	0.59	0.01	0.58	1.14	0.23	Matrix	3.41	7.25

The chemical analyses indicate that the plates are of unalloyed cast iron. The main elements in unalloyed cast iron are Carbon, Manganese, Phosphorus, Sulphur, and Silicon. The other elements are considered as impurities since they do not influence the properties.

The carbon equivalents (CE%) for the various materials were calculated using the following equation [8].

$$CE(\%) = C\% + 0.33Si\% + 0.33P\% \quad (2)$$

The CEs for the two cast iron plates are 3.65 and 3.41 for CAEL and NULUX, respectively. From Table 1, Mn:S ratios of the two plates are 5.33 and 7.25 for CAL and NUL, respectively. Figure 1 shows the microstructures of the two different cast iron mill-plates. Three phases can be identified in the micrographs: cementite (white) in a matrix of pearlite (black) and ferrite (grey) phases. The volume fraction of cementite, pearlite, and ferrite phases in CAL and NUL specimens are (44.85, 37.45, 17.70) and (39.86, 40.42, 19.72), respectively. For high cooling rate and a low CE, the formation of white cast iron is favoured whereas a low cooling rate and high CE promotes grey cast iron formation. White cast iron contains predominantly cementite (Fe_3C) phases whereas grey cast iron contains mainly free carbon in the form of graphite.

Assuming the cooling rates were the same, the tendencies for the materials to form white cast iron would be NUL and CAL in decreasing order. High fraction (> 1 wt.%) of silicon can graphitize cementite into iron and carbon. For Mn:S ratio of less than about 1.7, sulphur stabilizes cementite producing a white cast iron [9]. The ratios indicate that sulphur will not stabilize cementite directly. However, the high concentration of manganese will indirectly promote cementite formation.

Effect of Exposure Time on Weight Loss

Figure 2 shows the mass loss as a function of test periods for the different types of cast iron specimens. The mass loss data in this study are expressed as the mass loss per unit surface area. The mass losses recorded in CAL and NUL were about the same during the first three days of accelerated corrosion. After the third day, the mass losses recorded in CAL were higher than that of NUL until the end of the exposure test. It is interesting to know that from

the sixth to the ninth day of exposure time, the mass losses in both specimens decreased, indicating that the chemical reactivities at the specimen/solution interface were stifled.

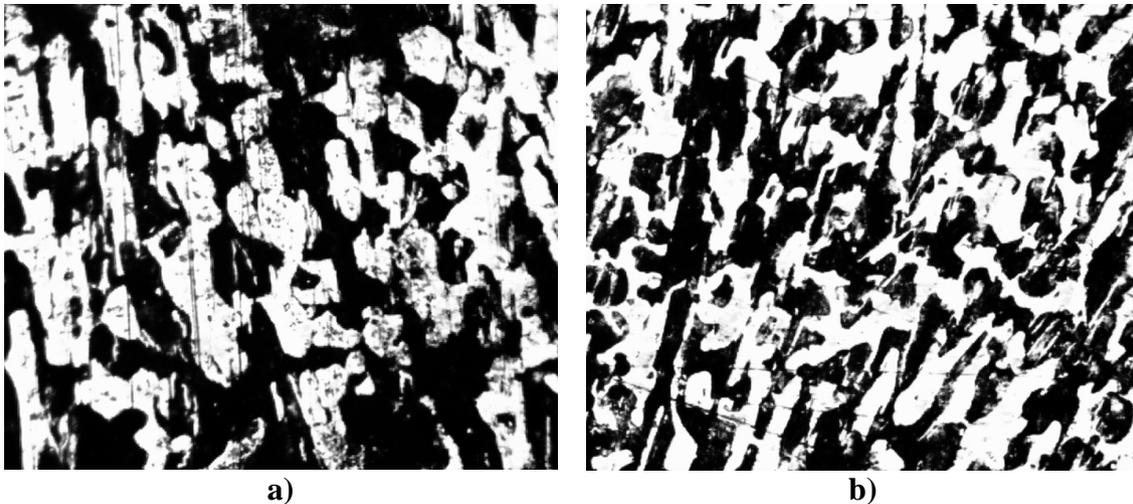


Figure 1. Photomicrographs of a) CAL, b) NUL cast iron mill-plates showing cementite (white), in a matrix of pearlite (black) and ferrite (grey) phases (100X, Nital etched).

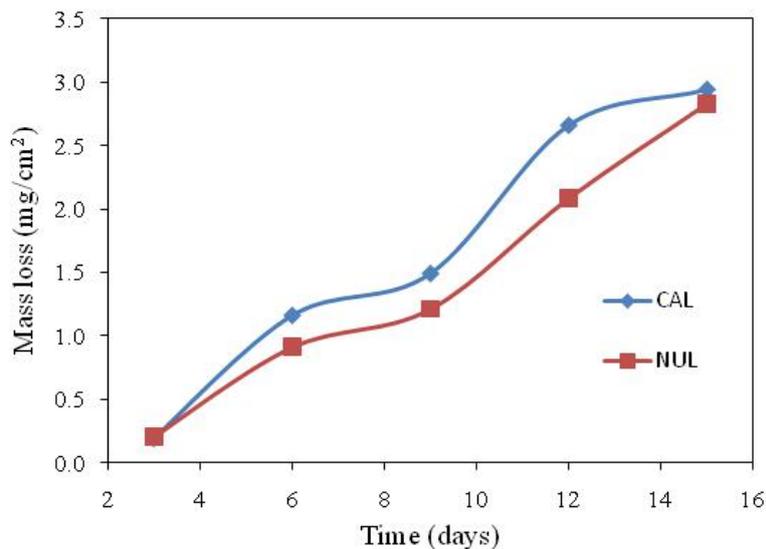


Figure 2. Weight loss versus exposure time of cast iron in electrolyte

Effect of Exposure Time on Corrosion Rate

The extent of susceptibility to corrosion in corrosive environments depends on several factors including the aggressiveness of chemical reactivities, velocity of environment, pH of the solution, the metallurgy of the alloy under study and temperature of the corrosion medium. In both cast iron specimens, increasing exposure time resulted in an increase in average corrosion rate (ACR) during the first six days of exposure time (Figure 3). The ACR's were determined according to Equation (2). CAL recorded a higher ACR compared to NUL specimens in the accelerated corrosion tests. ACR in both specimens decreased markedly

from the sixth day and then increased again in both specimens after the ninth day. ACR decreased slightly in CAL from the twelfth day until the end of the exposure test. There was no subsequent reduction in average corrosion rate in NUL after the ninth day. It must be emphasised here that the corrosion rates shown in Figure 3 are the average corrosion rates (ACR). To better understand the corrosion kinetics, it is important to consider instantaneous mass loss rate rather than using average mass loss data. Hence, the mass loss data obtained in Figure 2 were differentiated and the values plotted against time (Figure 4) giving the true corrosion rates. Thus, the instantaneous corrosion rates $R (= dy/dt)$, were determined using MATLAB 'gradient' functions as follows:

$$R = \text{gradient}(y, t) \quad (3)$$

where $y = M/A$ is the mass loss per unit area, and t is the time of exposure.

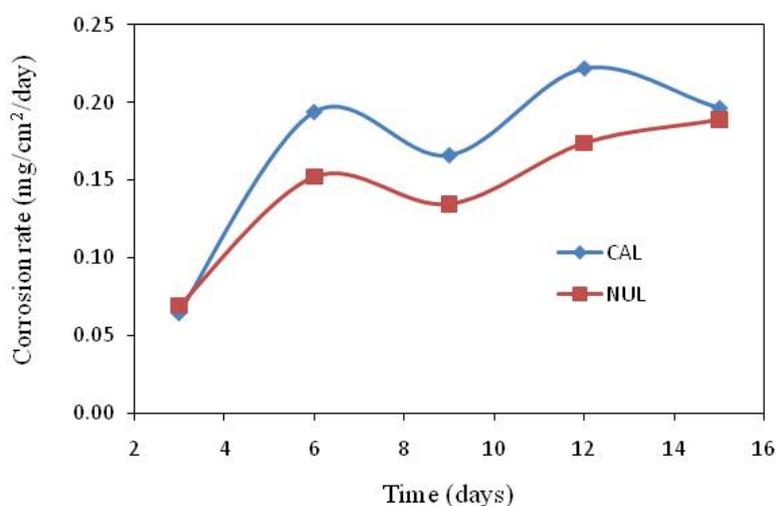


Figure 3. Average corrosion rate versus exposure time of cast iron in processed water

From Figure 4, the initial corrosion rates at day three of exposure time were high in CAL and NUL. The corrosion rate was, however, higher in CAL ($\sim 0.33 \text{ mg/cm}^2/\text{day}$) than in NUL ($\sim 0.24 \text{ mg/cm}^2/\text{day}$). The corrosion rates decreased in both specimens from the third day to the sixth day. The decrease in corrosion rate is due to one of two reasons. Firstly, decrease in corrosion rate may be due to the formation of an oxide layer which stifled the chemical reactivities at the specimen/solution interface. During this period where the corrosion rate decreased, the pH of the solution increased from acidic region to neutral/alkaline region. This transition is expected to stifle the chemical reactivities as well.

Secondly, the decrease in corrosion rates may also be attributed to a diffusion-controlled process, where transports of reactants are the rate determining step. The corrosion rates increased after the sixth day in both specimens due to either non-adherent of oxide layer

or absence of diffusion-controlled process as a result of the transition from the acidic to alkaline region. The corrosion rates decreased again after the ninth day in CAL and twelfth day in NUL.

Since the pH values recorded were in the alkaline region, the decrease in corrosion rates is due to the formation of an oxide layer.

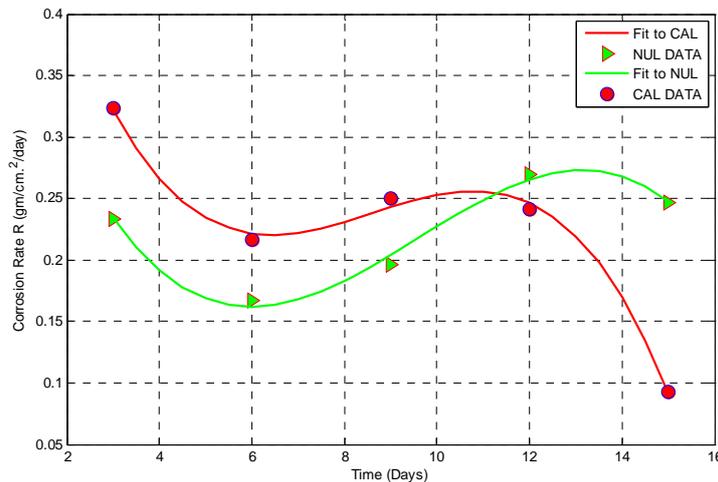


Figure 4. Corrosion rate ($R=dy/dt$) versus exposure time for the different cast irons.

Effect of Exposure Time on Ph

Formation of corrosion products that are protective is an important factor for corrosive-wear resistance of any material. Hard, dense, adherent, continuous films give good resistance, provided that they are not brittle and easily removed under stress. Solution pH affects protective films of many metals that exhibit passivity features. The effect of pH of the electrolyte on corrosion rates of cast iron grinding plates is shown in Figure 5. The pH increased with exposure time from acidic region to alkaline region at the end of the test period for all specimens.

The general increase in pH of the test solutions could be attributed to the action of microbial activities during the exposure time and also the corrosion process itself causing an increase in the amount of hydroxide ions in the solution. Visible corrosion products (i.e. rust) were observed on all corrosion specimens during the early stages of the immersion tests resulting in the changed pH values.

It is interesting to note that pH of the solution remained almost the same in CAL and NUL specimens during the first three days of exposure time. However, sharp increase in pH values were observed in CAL after the third day compared to NUL due to higher corrosion rate in CAL producing more hydroxide ions.

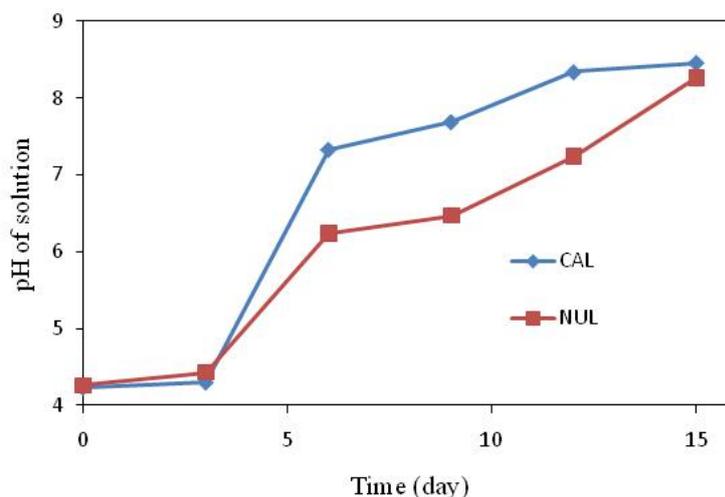


Figure 5. pH of corrosive medium versus exposure time of cast iron

Effect of Ph on Corrosion Rate

The effect of pH on corrosion rate is shown in Figure 6. In the corrosive environment selected, the corrosion rates of all the specimens were observed to be strongly dependent on the pH of the corrosion environment. Lower pH (acidity) implies the evolution of hydrogen or formation of H_2O and therefore preventing formation of any protective film. Corrosion rate decreased steadily in both specimens but increased after the sixth in both CAL and NUL. In acidic environment, the cathodic reaction can be described as follows:



In the presence of oxygen, equation (4) becomes:



Since the electrolyte was not deaerated, Equation (5) is the more likely cathodic reaction taking place in this corrosion studies.

For concentration-controlled process and at high reaction rates, cathodic reactions deplete the adjacent solution of the dissolved H^+ species. Concentration profile of H^+ ions in solution near the surface of a cathode is created, which could also lead to the decrease in the corrosion rate observed. Additionally, the decrease in corrosion rate could be due to the formation of an oxide layer, which stifled the corrosion process.

It is observed that corrosion rate decreased steadily to pH values greater than 6. From Fe- H_2O potential-pH diagram [10], at pH above 6, protective scale forms in the form of $Fe(OH)_2/Fe(OH)_3$ which hinder mass transport of oxygen and ionic species in the solution. It is evident from Figure 6 that pH increased faster in CAL than in NUL solution. For instance, from an initial pH of 4.2, it took NUL twelve days to reach pH of about 7.2 whereas in CAL, it only took six days to reach pH of about 7.3. This is due to an increased corrosion rate in

CAL (~0.05 order of magnitude) forming more hydroxide ions in solution than in NUL (Figure 4).

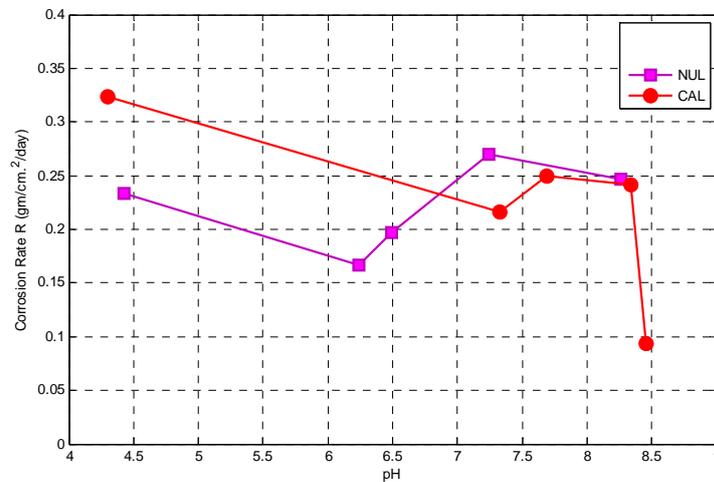


Figure 6. Corrosion rate versus solution pH of cast iron materials

Relationship of microstructure to corrosion behaviour

Cast iron studied consisted of multiphase structure consisting of cementite in a matrix of pearlite and ferrite phases. Assuming that there is no setup of electrolytic cell between the phases, the following reactions are possible: the anodic reactions in ferrite and cementite are respectively:



The cathodic reaction in acidic solution could be described by Equation (5). In neutral and alkaline solution, the cathodic reaction could be described as follows:



If there is an electrolytic cell between the ferrite and cementite, then the cementite becomes the anode. Ferrite phase is noble due to the fact that it contains a small amount of carbon atoms interstitially dissolved in it (maximum 0.02 wt% C). This makes it more corrosion resistance in comparison to the cementite phase which has a greater proportion of carbon addition and is also metastable [11]. Within a pearlite grain where ferrite and cementite coexist, cementite would preferentially corrode for the same reasons stated above. Imperfections in materials associated with higher energies tend to be more susceptible to corrosion. Therefore, Equation (7) is the more likely reaction to contribute to the measured corrosion rate. The volume fractions of the phases in the microstructure have been calculated and presented earlier under section 3.2. It showed that cementite/pearlite volume ratio is

higher in CAL (1.20) than in NUL (0.99). From the volume ratios, corrosion rate is expected to be high in CAL than in NUL. This is due to the high anode/cathode volume ratio. In the case of NUL specimen, the volume ratio of cementite: pearlite is almost 1:1, hence the area effect on galvanic corrosion would not be apparent [11, 12]. From Fe-Fe₃C phase diagram, the volume fraction of cementite in pearlite for cast iron microstructure is estimated to be 12%. This means that electrolytic cell could be set-up within the pearlite grain when all the cementite phases in the microstructure have been attacked. When this happens, it would be expected that the CAL specimen would be attacked more than the NUL since CAL has got high volume fraction of the pearlite phases in the microstructure.

Contribution of Corrosion to Wear

From the results obtained, it can be inferred that cast iron grinding plates would wear faster in wet grinding due to the tendency to form oxide layer, which would result in corrosive wear in addition to the abrasive wear. Wear is assumed to be affected by corrosion only in regions where protective oxide layer forms. The pH of the corrosive environment increases with time from acidic to alkaline environments, where the tendencies to form any protective layer exist. The grinding mechanism of maize (corn) in corn-mill machines causes surface interaction between the two milling plates and the maize that is being processed. This surface interaction would erode the corrosion products which will subsequently contribute to an increase corrosion rate as it exposes fresh surfaces for corrosion to occur. Subsequent contamination of the milled corn is inevitable. Consumption of the corrosion products could impact on the health of consumers as the form of the oxide consumed could be insoluble and therefore deposits in the liver. For instance, iron from ferrous salt is more readily absorbed than in ferric salts and ionisable forms of iron are more readily absorbed than elemental iron, ferric hydroxide and iron oxides [13]. This could cause serious health problems such as infection of the liver [14, 15].

Conclusions

Cast iron mill-plates are susceptible to corrosion attack. Corrosion rate largely depends on chemical composition, microstructure and pH of the corrosive environment. Average corrosion rates were higher in CAL than in NUL during the exposure period. This is due to the different volume fractions of cementite-pearlite-ferrite phases. The instantaneous



corrosion rates determined from the mass loss measurements assisted in explaining the corrosion behaviour in both materials. The decrease in corrosion rates at low pH (acidic) in both materials could be as a result of corrosion products formation or diffusion-controlled processes, where concentration profile of H^+ ions in solution near the metal interface were created. At high pH (alkaline), decreased in corrosion rates were as a result of a formation of an oxide layer whilst an increased corrosion rates were as a result of the non-adherent of the oxide layer formed on the material surfaces. The corrosion products were therefore removed exposing fresh surface for corrosion to continue. In wet grinding, the cast iron material would wear faster than in dry grinding due to corrosive-wear mechanism in the former since corrosive-wear strongly depends on oxide layer formation and hence the pH of the corrosive environment. The contamination of iron (Fe) in the milled maize when consumed could lead to iron overload in humans, which can cause serious health problems. Therefore from material development point of view a suitable material for maize (corn) milling is one with combination of wear and corrosion resistances. This may be achieved by addition of chromium with the objective of forming hard and wear-resistance carbides as well as forming corrosion-resistance oxides.

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