

COMBINED EFFECT OF ABRASION AND CORROSION ON THE WEAR OF CAST IRON GRINDING BALLS WITH CHROMIUM CONTENTS FROM 12 TO 30%¹

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Abstract

The wear rates of high chromium cast iron grinding balls were measured in an ore grinding pilot-plant, simulating the operation of an industrial plant producing finely ground iron ore used as pellet feed. Iron ores with silica contents of 2 and 7% were used in the tests. The pH of the process water was either 7.2 or 8.5. In the higher pH condition, the lowest wear rate was obtained for a 24%Cr-3.0%C alloy, with high percentage of eutectic carbides in the microstructure. In the more corrosive environment, at pH 7.2, the best performance was shown by a 30%Cr -2.2%C alloy in spite of its lower carbide content and lower hardness. Comparing tests at pH 7.2, the increase of the silica content from 2 to 6% resulted in higher wear rates for all alloys and markedly reduced the performance difference among the various alloys. This result was attributed to the predominance of the abrasion effect over the corrosion effect.

Key words: Grinding balls; Abrasion-corrosion; High chromium cast iron.

EFEITO COMBINADO DE ABRASÃO E CORROSÃO NO DESGASTE DE BOLAS DE MOINHO COM TEORES DE CROMO ENTRE 12 E 30%

Resumo

As taxas de desgaste de bolas de moinho de ferro fundido de alto cromo foram determinadas por meio de ensaios em planta piloto de moagem, simulando a operação de moagem fina de minério de ferro utilizado para a produção de pelotas. Nos ensaios, foram utilizados minérios de ferro com teores de sílica de 2% ou 6% e o pH da água de processo foi de 7,2 ou 8,5. Na condição de pH elevado, as menores taxas de desgaste foram obtidas no ensaio com uma liga 24%Cr-3,0%C, com altas porcentagens de carbonetos eutéticos na microestrutura. No ambiente mais corrosivo, com pH de 7,2, o melhor desempenho foi proporcionado por bolas de moinho da liga 30%Cr -2,2%C, apesar da menor quantidade de carbonetos e menor dureza dessa liga. Em ensaios com o pH 7,2, o aumento do teor de sílica de 2 para 6%resultou em grandes aumentos das taxas de desgaste de todas as ligas e uma concomitante diminuição da diferença de desempenho entre as várias ligas. Isso foi atribuído à predominância do efeito de abrasão sobre o efeito de corrosão, na condição de elevado teor de sílica.

Key words: Bolas de moinho; Abrasão-corrosão; Ferro fundido de alto cromo.

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1 INTRODUCTION

The synergy between abrasion and corrosion mechanisms strongly affects the performance of high chromium cast iron in grinding and similar operations. (1-11) In many cases, the synergy involves the abrasive removal of passivation layers, allowing the corrosion process to continue. Increasing the resistance and adherence of these layers to the base alloy improves the overall wear resistance. (12,13) Interphase corrosion is particularly relevant for high chromium cast irons. (14) High Cr carbides are cathodic in relation to the adjacent matrix, leading to its corrosion. A chromium depletion in this region, as usually observed in cast parts, intensifies this mechanism.

High chromium cast irons resistant to simultaneous abrasion and corrosion actions must attend a set of requirements including:

- a) High Cr content dissolved in the matrix;
- b) Martensite hardness in the range of 700 HV;
- c) Low retained austenite content and complete absence of pearlite;
- d) Eutectic carbides contents in the range 20-30%; and
- e) Formation of strong and adherent passivation layers and fast repassivation.

This paper presents results of wear rates for high chromium cast balls with varied chemical compositions, under different combinations of abrasivity and corrosivity of iron ore slurries, in tests conducted in a pilot-plant and in an industrial plant.

2 MATERIALS AND METHODS

The wear resistance of alloys with various Cr contents was evaluated by means of tests in ball mills, during wet grinding of iron ores. Tests were performed in a pilot-plant and in an industrial plant.

The basic characterization of the tested balls comprised the chemical analysis, Rockwell C hardness and HV_{100} matrix microhardness (100g load).

2.1 Tests in Grinding Pilot-Plant – 1st and 2nd Series

The grinding pilot-plant simulates the operation of an industrial plant, fed with an iron ore sample supplied by a major mining company. It is a continuous pilot plant equipped with a ball mill and a hydrocyclone classifying system (Table 1).

The materials and conditions used in the first and second series of experiments are presented in Table 2. The ball samples in the 1st series came from commercial production and were designated as GB1 to GB7. The second series comprised two commercial alloys selected as "best performers" in an industrial application, namely GB7 (as in the 1st series) and GB10 and four experimental alloys. The basic characteristics of the alloys of the tested balls are presented in Table 3. Previously to the first wear test, sample of the alloys were evaluated as to their corrosion response in polarization tests. The two steels showed pitting corrosion, the two cast irons with the lowest Cr contents presented preferential corrosion of the matrix and the two higher Cr alloys were passivated.

The wear rates in the pilot plant tested were determined as follows:

 a) 10 to 20 balls of each type were marked and submitted to run-in using quartz sand;



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- b) The balls were cleaned, dried, individually weighed to 0.01g and loaded in the mill (the charge of the mill is completed with non-marked balls).
- c) Along the test, the balls were removed, cleaned and weighed after each 10 to 12 h of milling.
- d) The mass loss at each period was determined and converted to equivalent diameter loss. At the end of the test, a straight line "diam. X time" was obtained for each ball. The slopes of these lines are the respective "wear rate" for each ball. The value was averaged for each ball group and presented in the tables to follow.

The results of the 1st and 2nd series of tests in the pilot-plant are presented in Table 7.

Table 1 - Dimensions and operation parameters of the grinding pilot-plant

| Parameter | Value |
|-------------------------------------|-----------------|
| Ball mill (inner diameter x length) | 0.38 m x 0.38 m |
| Ball charge | 70.9 kg |
| Mill lining | Rubber |
| Speed (75% of the critical speed) | 53 rpm |
| Solids in slurry | 80% wt |
| Feeding rate (dry basis) | 74 kg/h |
| | |

Table 2 - Materials and conditions in the 1st and 2nd series of experiments in the pilot-plant

| Parameter | Va | lue |
|-----------------------------|------------------------|------------------------|
| | 1 st series | 2 nd series |
| Size analysis (ore feeding) | 92% < 75μm | 92% < 75μm |
| Silica content of the ore | 2.6% | 2.6% |
| Process water pH | 9.0 | 8.0 |
| Time of grinding | 56 h | 35 h |

Table 3 - Characterization of the materials of the halls of the 1st and 2nd series

| Table 3 - Characterization of the materials of the balls of the 1 - and 2 - series | | | | | | |
|--|------|---------|---------|--|-------|---------------|
| Type | Comp | osition | | Microstructure | | Hardness |
| | %C | %Cr | matrix | Eutectic carbides (type; %) | HRC | microhardness |
| GB1 | 3.47 | 0.34 | P* | M ₃ C ; 42% | 52 | 530 |
| GB2 | 2.73 | 25.0 | M* | M_7C_3 ; 30% | 62 | 720 |
| GB3 | 0.86 | 0.22 | M | None (forged steel) | 66 | 840 |
| GB4 | 3.00 | 11.0 | M | M_7C_3 ; 26% | 62 | 700 |
| GB5 | 3.00 | 30.0 | М | M ₇ C ₃ ; 31% (partially pro- eutectic carbides) | 59 | 680 |
| GB6 | 1.19 | 0.59 | M + RA* | None (forged steel) | 58 | 730 |
| GB7 | 2.17 | 33.3 | M | M_7C_3 ; 17% | 62-64 | 770 |
| GB10 | 2.22 | 30.1 | M | M_7C_3 ; 20% | 62-64 | |
| EXP30-A | 2.3 | 30 | M | M_7C_3 ; 20% | 62-63 | 740-760 |
| EXP30-B | 2.2 | 31 | M | M_7C_3 ; 20% | 62-63 | |
| EXP30-C | 2.2 | 31 | M | M_7C_3 ; 20% | 62-63 | 740-760 |
| EXP25 | 3.0 | 25 | M | M_7C_3 ; 30% | 64-66 | 740-760 |

^{*} P=Pearlite; M=Martensite; *RA=Retained Austenite



2.2 Tests in the Industrial Grinding Plant

Based on the results of the pilot-plant tests, a marked ball test was performed in an industrial plant, in which balls of the GB10 type is successfully used. Balls of the EXP30-A and EXP25 types were included. Besides the size of the mill, the main difference in the grinding condition in comparison with the pilot-plant tests was the pH and ions contents of the respective process waters, as shown in Table 4.

Two tons of marked balls of each experimental type were charged together with the standard GB10 balls and samples were collected from the mill after 1,800h. A second test in the industrial plant was run after some improvement in the quality of the 30%Cr balls, leading to the development of the EXP30-C type. The results of the tests in the industrial mill are presented in Table 8.

Table 4 - Characteristics of the process water: pilot-plant vs. industrial plant

| | acteristics of the process we | Value | |
|-------------------------------|--|------------------|--|
| Parameter | Pilot-plant | Industrial plant | Pilot-plant |
| | (1 st and 2 nd series) | | (3 rd and 4 th series) |
| pН | 8.0-9.0 | 7.0 to 7.6 | 7.1 |
| Chlorides(Cl) | 5.8 mg/L | 18 mg/L | 300 mg/L |
| Fluorides(F ⁻) | 0.7 mg/L | 0.8 mg/L | 0.7 mg/L |
| Ca | 81 mg/L | 12 mg/L | 81 mg/L |
| HCO ₃ ⁻ | 21 mg/L | 46 mg/L | nd |

2.3 Tests in Grinding Pilot-plant – 3rd and 4th Series

For the 3rd and 4th series of tests in the pilot-plant, the process water was conditioned in order to produce corrosion effects similar to those observed in the tests in the industrial mill. Hydrochloric acid (HCl) sufficient to reduce the pH to 7.1, and 0.53 g/L of NaCl were added to the process water. Preliminary tests in a batch mill confirmed that in this condition the ranking of performance of the balls tended to be similar to that observed in the industrial mill. The main difference between the ores used for either the 3rd or the 4th test series was the silica content, which was much higher in the 4th test. The conditions for the 3rd and 4th tests are shown in Table 5.

The balls tested in the 3rd series consisted of commercial products made of cast irons with Cr contents ranging from 12 to 30%. In the 4th series some experimental alloys were tested. About twenty balls of each type were charged in the mill. The main characteristics of the tested materials are presented in Table 6.

Table 5 - Materials and conditions for the 3rd and 4th series of experiments in the pilot-plant

| Table 5 - Materials and conditions for the 5 | and 4 Series of experiments in | the phot-plant |
|--|--------------------------------|------------------------|
| Parameter | Va | lue |
| | 3 rd series | 4 th series |
| Size analysis (ore feeding) | 95% < 75μm | 98% < 75μm |
| Silica content of the ore | 2.2% | 6% |
| Process water pH | 7.1 | 7.1 |
| Time of grinding | 56 h | 50 h |

Table 6 – Chemical composition and hardness of balls in 3rd and 4th tests

| Source | Material | | Basic chemical composition | | Tests | |
|--------------|----------------|------|----------------------------|----------|-----------------|-----------------|
| | Identification | %Cr | %C | HRC | 3 rd | 4 th |
| | Forged steel | 0.32 | 0.76 | 49 to 56 | yes | yes |
| | GB10 | 30.1 | 2.22 | 63.0 | yes | no |
| Commercial | GB113 | 11.3 | 3.20 | 66.3 | yes | no |
| alloys | GB223 | 22.3 | 2.95 | 65.5 | yes | yes |
| | GB253 | 25.3 | 2.84 | 64.8 | yes | yes |
| | GB300 | 30.0 | 2.30 | 63.5 | yes | yes |
| | IPT-30HT | 30.7 | 2.30 | 62.8 | yes | yes |
| Experimental | IPT-MS7 | 15.2 | 0.72 | 58.6 | yes | no |
| | IPT-MS5 | 15.0 | 0.57 | 57.0 | yes | no |
| | IPT-22Cr | 22.8 | 2.05 | 62.5 | yes | yes |

The results of the 3rd and 4th series in the pilot-plant are presented in Table 9.

3 RESULTS AND DISCUSSION

The results of the wear tests are presented in Tables 7 to 9. The results of the first series of tests in the pilot-plant show that the higher wear resistance is obtained with a balanced combination of the amount of hard eutectic carbides, high matrix microhardness and high Cr content in the matrix. The two best performances were obtained by the GB7 and GB2 balls. These materials have in common high matrix hardness over 700 HV. The carbide content of the GB2 alloy is higher, while the Cr content in the matrix is much higher for the GB7 balls, which presented the best result of all. The worse performance corresponded to the materials with the lowest Cr contents, regardless of the hardness values: GB1, GB3 and GB6. The result for the GB3 steel shows that hardness alone is not a guarantee of good performance. The importance of high Cr content in the matrix is demonstrated by the result for alloy GB4. The high hardness and high carbide content were not sufficient to impart a good performance to this alloy, which has only about 3% Cr dissolved in the matrix. From the carbide volume fraction, high Cr content and high microhardness, a good result could be expected for the GB5 balls, but its performance was poor. The reason for this is that this alloy resulted hypereutectic with coarse primary carbides, a condition that favors the microcracking abrasion mechanism, with high rates of mass loss.

The results in the 1st series inspired the development of the alloys tested in the 2nd series. Balls GB7 and GB10 (a commercial variation of GB7) were used as reference. EXP30Cr-A and EXP30Cr-B were laboratory versions of the commercial alloys, with 0.5Nb added in the later. Since the only available information on the production process of the commercial balls was the analyzed basic chemical composition, this test aimed to verify the success of the laboratory in reproducing the successful alloy, considering other aspects, like the heat treatment and minor elements



contents. EXP25Cr alloy tried to optimize the microstructure and hardness, compared to the GB2 alloy.

The 30%Cr experimental alloys presented results comparable to those of the commercial alloys, but the performance of the 25%Cr alloy was surprising, with 40% less mass loss than the other materials.

The values for the Cr contents in the matrix of the alloys were calculated for the typical heat treatment temperature of each alloy, using the computational thermodynamics software Thermocalc, with TCFE6 data base. This method has been used successfully to estimate the composition of the matrix of complex alloys. (15-17)

The general tendency of the effect of the Cr content in the matrix on the wear rates is shown in figure 1 (the result of alloy GB5 was excluded because of the predominance of the microstructure effect).

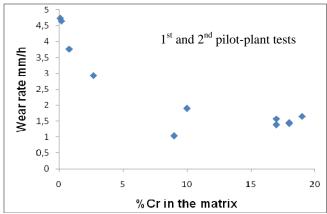


Figure 1 – Effect of the Cr content in the matrix on the wear rate of balls.

The success of the test in the pilot-plant led to testing the experimental alloys in an industrial mill. As shown in Table 8, in the first test in the industrial mill, both alloys – Exp30-A and Exp 25 – failed to obtain a performance comparable to that of the 30%Cr commercial alloy, since the measured wear rates of the experimental balls were 30 to 40% higher, as compared to historical values. Observations of the surface of the tested balls showed that corrosion was occurring, especially in the EXP25 balls as can be seen in figure 2. It was concluded that the industrial process water created a much more aggressive environment than the one used in the pilot-plant test. This led to the 3^{rd} and 4^{th} series of experiments in the pilot-plant.



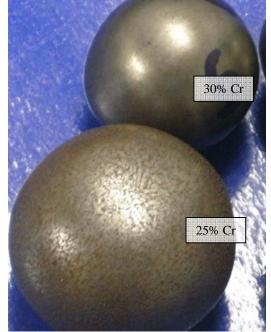


Figure 2 – Aspect of Exp30-A and Exp 25 balls after test in the industrial mill.

In the 3rd series of experiments in the pilot-plant the process water was modified in order to become more aggressive to the alloys, in terms of corrosion. The iron ore was similar to that used in previous tests. Comparing the wear rates of the 3rd series – Table 9 - with those corresponding to the two first series - Table 7, it is clear that all but the 30%Cr alloys were affected by the more corrosive environment. For the 30%Cr balls, the wear rates were in the range 1.4 to 1.6 µm/h in the 1st and 2nd series and 1.1 to 1.2 μm/h in the 3rd series. On the other hand, the wear rates of the steel balls increased from 4.7 to 5.1 μ m/h and those of the 11%Cr cast irons, from 2.9 to 3.5 μ m/h. The most important result in this series refers to the wear rates of the 25%Cr alloys. These alloys ranked among the best performances in the previous tests, with the EXP25Cr presenting the best of all results. However, the performance of the balls with 25%Cr in the industrial mill was poor. In the more aggressive process water of the 3rd experiments the range of wear rates of the alloys with 22 to 25%Cr and high carbon increased to the range 1.8 to 2.1 μm/h, a very sharp increase in comparison with the 1.04 μm/h wear rate of the 2nd series for a similar alloy.

The effect of the %Cr dissolved in the matrix of the alloys is also seen in the results of the matrix steels with 25%Cr, with much better results than the carbon steel, as well as those of the 22%Cr alloy with reduced C content. All these results show that in the case of a very aggressive process water, corrosion may be at least as important as abrasion as an wear factor. On the other hand, the cast irons still perform better than the steels, showing that the hard eutectic carbides are necessary to limit the abrasion process.

From all the results, the experimental alloy IPT-30HT with 31%Cr and extended heat treatment time showed the best performance. The more uniform Cr distribution in the matrix obtained by means of the extended heat treatment is the most probable



cause for this. This result led to the production of the sample for tests in the industrial mill designated as EXP30-C.

The results of the 2nd test in the industrial mill are shown in Table 8. The improved experimental 31%Cr balls had a performance comparable to the best one obtained in the history of the mill, while the 25%Cr balls performed even worse than in the 1st test.

The results of the 4th series of tests in the pilot-plant, corresponding to the use of an iron ore with high silica content showed that increasing the abrasion effect leads to a general increase in the wear rates. However the most important result of this series is that the difference in performances between the 30%Cr alloy and the other alloys is much less in this condition of higher abrasivity of the ore. In commercial terms, considering its high cost, the 30%Cr alloys will be more competitive only in a high corrosion-low abrasion condition.

A summary of the most important results is given in Table 10 and in the graph of Figure 3. The steel presented the highest wear rate in all cases, and its wear rate increased gradually as the conditions became more severe. The 25%Cr alloys with high C content had excellent performance in the least severe condition, but were strongly affected by corrosion in the low pH condition. On the other hand, increasing the silica content of the ore did not cause a very important loss of performance of this group of alloys. Decreasing the C content of the alloys in this range of Cr content was beneficial to the corrosion resistance, but detrimental to the abrasion resistance.

Balls of the 30%Cr alloy had the best performance in the corrosive conditions, but were strongly affected by the rise in the silica content.

Table 7 – Wear rates in the pilot-plant 1st and 2nd series

| Material | Chemical Composition and microhardness | | | Wear Rate (μm/h) | | |
|-----------|--|------|---------|------------------------|------------------------|--|
| | %C | %Cr | μΗ | 1 st series | 2 nd series | |
| GB1 | 3.47 | 0.34 | 530 | 4.73 | | |
| GB2 | 2.73 | 25.0 | 720 | 1.90 | | |
| GB3 | 0.86 | 0.22 | 840 | 4.64 | | |
| GB4 | 3.00 | 11.0 | 700 | 2.93 | | |
| GB5 | 3.00 | 30.0 | 680 | 2.96 | | |
| GB6 | 1.19 | 0.59 | 730 | 3.76 | | |
| GB7 | 2.17 | 33.3 | 770 | 1.65 | | |
| GB10 | 2.22 | 30.1 | 770 | | 1.45 | |
| GB7 | 2.17 | 33.3 | | | 1.39 | |
| EXP30Cr-A | 2.2 | 31.0 | 740-760 | | 1.57 | |
| EXP30Cr-B | 2.2 | 31.0 | | | 1.43 | |
| EXP25Cr | 3.0 | 25.0 | 740-760 | | 1.04 | |



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Table 8 – Wear rates in the industrial mill (fine iron ore grinding)

| Sample | Wear Ra | te (μm/h) |
|------------------------|----------------------|----------------------|
| | 1 st test | 2 nd test |
| Reference charge, GB10 | 2.5-2.9 | 2.5-2.9 |
| EXP30Cr-A | 3.46 | - |
| EXP25Cr | 3.80 | 4.90 |
| EXP30Cr-C | | 2.53 |

Table 9– Results of the 3rd and 4th experiment in the pilot-plant

| Source | Identification | | Basic chemical composition | | Wear rate (μm/h) | |
|---------------------|----------------|------|----------------------------|------------|------------------|--|
| | | %Cr | %C | 3rd series | 4th series | |
| | Forged steel | 0.32 | 0.76 | 5.09 | 5.31 | |
| | GB10 | 30.1 | 2.22 | 1.24 | nt* | |
| Commoraid | GB113 | 11.3 | 3.20 | 3.52 | nt | |
| Commercial | GB 223 | 22.3 | 2.95 | 1.76 | 2.42 | |
| | GB253 | 25.3 | 2.84 | 2.07 | 2.38 | |
| | GB300 | 30.0 | 2.30 | 1.23 | 2.24 | |
| - | IPT-30HT | 30.7 | 2.30 | 1.10 | 1.99 | |
| Experimental alloys | IPT-MS7 | 15.2 | 0.72 | 2.37 | nt | |
| | IPT-MS5 | 15.0 | 0.57 | 2.43 | nt | |
| | IPT-22Cr | 22.8 | 2.05 | 1.59 | 2.66 | |

*nt=not tested

Table 10 – Summary of main effects on the wear rates

| Conditions | | V | Vear rates (μm/ | h) | |
|------------------|---------|------|-----------------|------|---------|
| Conditions | 25Cr-HC | 30Cr | steel | 11Cr | 23Cr-LC |
| Low SiO2/High pH | 1.04 | 1.46 | 4.64 | 2.93 | |
| Low SiO2/low pH | 1.92 | 1.19 | 5.09 | 3.52 | 1.59 |
| High SiO2/low pH | 2.40 | 2.12 | 5.31 | | 2.66 |

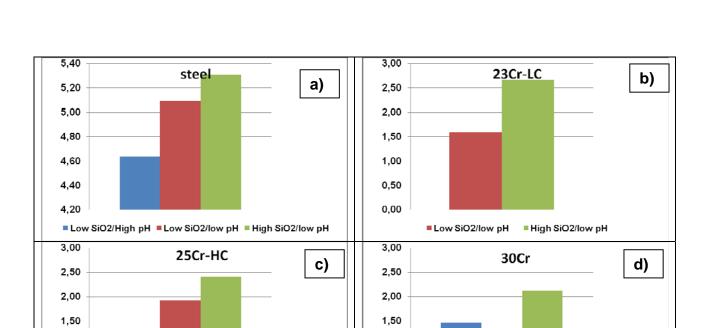


Figure 3 – Summary of main effects on the wear rates.

1.00

0,50

0,00

■Low SiO2/High pH ■Low SiO2/low pH ■High SiO2/low pH

4 CONCLUSIONS

■ Low SiO2/High pH ■ Low SiO2/low pH ■ High SiO2/low pH

1,00

0.50

0.00

The performance of high chromium cast iron balls during wet milling of iron ores is affected by the combination of corrosivity and abrasivity of the ore slurry. Alloys with 25%Cr and high eutectic carbide fraction presented the best performance in the condition with high pH and low aggressive ions content. With pH near 7 and high content of aggressive ions, the best performance was achieved by cast irons with more than 15%Cr dissolved in the matrix.

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