

## BEHAVIOR OF HIGH-SILICON CAST IRON UNDER WEAR AND CORROSION

Danilo Borges Villarino de Castro, [daniobvc@yahoo.com.br](mailto:daniobvc@yahoo.com.br)  
Artur Mariano de Sousa Malafaia, [arturdesousa@hotmail.com](mailto:arturdesousa@hotmail.com)  
Maurício Angeloni, [mauricio\\_angeloni@yahoo.com.br](mailto:mauricio_angeloni@yahoo.com.br)  
Luciana Sgarbi Rossino, [lsr@sc.usp.br](mailto:lsr@sc.usp.br)  
Omar Maluf, [omarramo@sc.usp.br](mailto:omarramo@sc.usp.br)

Department of Materials, Aeronautic and Automotive Engineering / Engineering School of São Carlos / University of São Paulo – Trabalhador São Carlense Avenue, 400; São Carlos/SP; Brazil.

**Abstract:** *The aim of this paper is to study the behavior of high-silicon cast iron regarding wear and corrosion. These alloys, basically ternary, Fe-C-Si, are recommended for applications where high resistance to corrosion is required for presenting in the material surface a protector coating of hydrated silicon oxide. This strength improves as the sum of silicon is increased so that reaching the best results on the range of 14.20 to 14.75% on weight. Two alloys of this type were studied and distinguished by amounts of chrome: 0.11% and 4.16% on weight. The wear strength of these alloys were assessed through tests of abrasion/erosion under conditions assembled by several types of slime, where the first corresponds to a less severe corrosive medium made of water and alumina then adding  $H_2SO_4$  in the second medium and other two different conditions with distinct concentrations of  $HNO_3$ . Although the corrosion strength of both studied alloys were assessed through tests of loss of mass by immersion in corrosive medium of 20% of  $H_2SO_4$  and 65% of  $HNO_3$ . For  $HNO_3$ , the analysis were made considering a time of immersion of 144 hours while the  $H_2SO_4$  condition the analysis were made in two different times of immersion: 72 and 144 hours consecutively. It was observed that, no matter the medium used, the material with less concentration of chrome presents lower wear strength. The increment of chrome results in the formation of a large amount of chrome carbides that increases considerably the material hardness thus increasing its wear strength properties. The more aggressive the corrosive medium gets the more pronounced becomes the difference in the loss of mass among the studied alloys. The corrosion strength for alloys with more chrome proved to be superior to the alloy with less chrome in the used medium:  $H_2SO_4$  and  $HNO_3$ . It might be related to the chrome characteristics of forming a passive coating in the surface of the material, by forming a protective layer of an adherent and fine oxide against additional corrosions. If damaged, the protective layer usually regenerates itself very quickly. It is important to mention that, even though the alloy with less concentration of chrome was less strength, it was still effective under corrosion strength tests as the super alloy made of cast nickel, which final cost is twenty times higher when compared to the presented studied alloy. For this reason, the alloy with less concentration of chrome may be recommended to be used in less aggressive medium since the less concentration of chrome has a low cost production if compared to the alloy with more concentration of chrome.*

**Keywords:** cast iron. Silicon. Chrome. Corrosion. Wear. Erosion.

### 1. INTRODUCTION

High-silicon cast iron are basically ternary alloys Fe-C-Si recommended for applications which high corrosion strength is required, such characteristic is achieved through the building of a protective coating of hydrated silicon oxide on the material surface (Mechura, 1970). This strength is improved as the amount of silicon increases, reaching the best results in the range of 14.20 to 14.75% of this element (Hurst, 1943). The rate of corrosion of high-silicon cast iron alloys influenced by sulfuric and nitric acids in several concentrations and temperatures and its benchmarking comparison with other alloys are exemplified in the Figs 1(a) and 1(b), respectively. The corrosion degree is shown in milimeters of acid penetration per year (ASM International, 1990; Iron Casting Society, 1981).

However, the mechanical properties are proportionally damaged to the increase of silicon. The low mechanical strength of this material compared, for instance, to the ordinary gray cast iron is explained by the presence of graphite ( $Fe+Fe_3Si_2$ ) precipitated in roughly solid solution and carbides ( $Fe + Fe_3Si_2 + C$ ) in its microstructure (Mechura, 1970). Silicon over 3% affects the properties and distribution of components in the microstructure and, due to its ferric characteristics, it promotes the decreasing of carbon in the eutectic thus promoting the formation of graphite during the solidification. Cast iron composed by 14 to 17% silicon, the ferrite matrix is displayed saturated by silicon and streaks of graphite, for carbon concentration between 0.40 and 1.00%. A commercial alloy with about 15% of silicon under the room temperature presents low mechanical and thermal strength as these values are the half from those presented by a high quality gray cast iron. Hence its use is limited to situations where corrosion and wear strength is required.

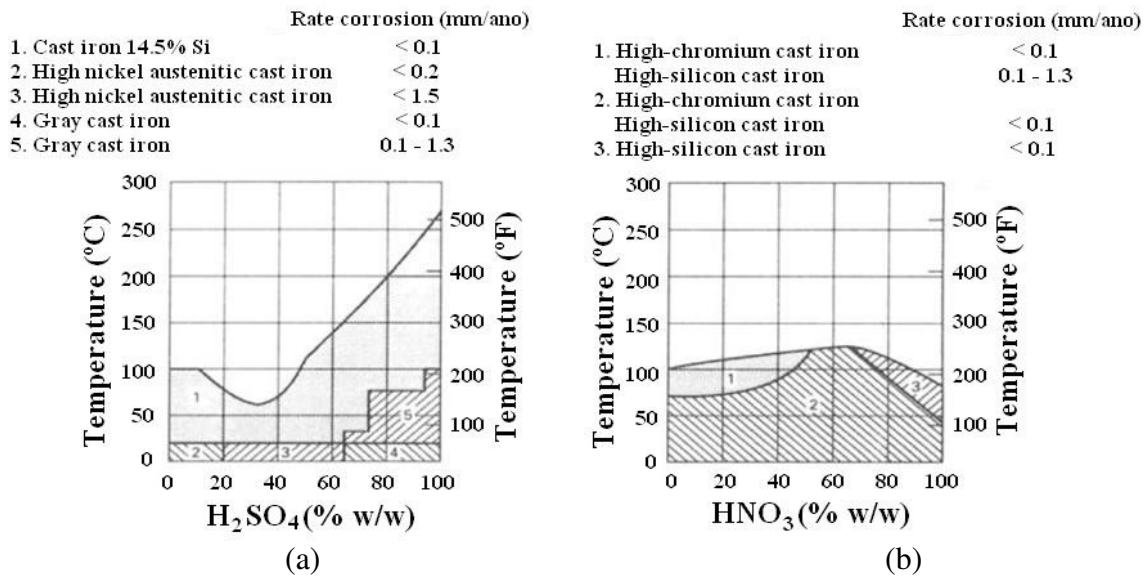


Figure 1. Corrosion strength of cast irons combined and not-combined in acidic medium in function of temperature and concentration of (a) sulfuric acid medium and (b) nitric acid medium (Iron Casting Society, 1981)

The corrosion strength of the high-silicon cast iron is not effective when the material is influenced by halogens and halogen acids. Figure 2(a) shows that the onset of concentrated hydrochloric acid at 90°C is estimated while in room temperature the corrosion degree is not accountable. The addition of molybdenum under the same conditions increases fundamentally the alloy corrosion strength with 15% of silicon. Figure 2(b) shows the results of the study of corrosion strength of the cast iron with 15% of silicon which contains 3.5% of molybdenum, compared to the same alloy without molybdenum in hydrochloric acid (70%) in boiling temperature. The corrosion strength is expressed as loss in milligrams per square centimeter (cm<sup>2</sup>). As a way of comparison, it is showed the alloy strength curve with 15% of silicon to sulfur acid (20%) in boiling temperature (Hurst, 1943).

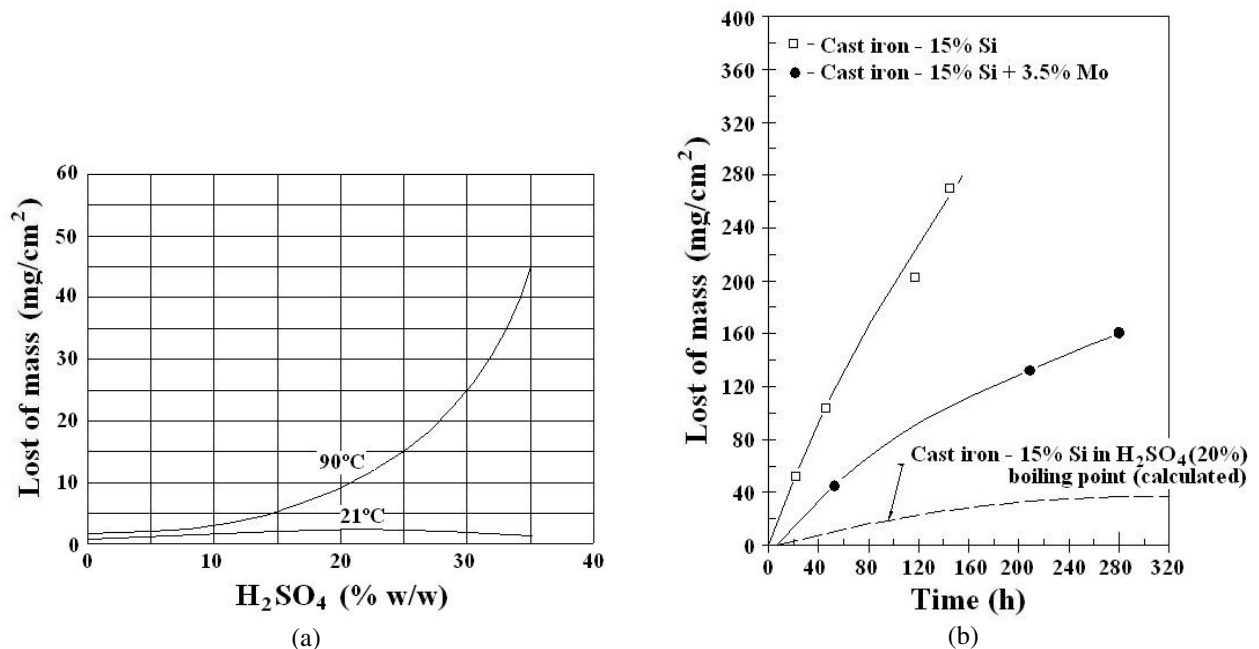


Figure 2. HCl corrosion in the high-silicon cast iron: (a) 8 hours trial in midst of solution with several stirred concentrations, hot and cold and (b) HCl solution 70% in boiling temperature (Hurst, 1943)

Another alloy element used mainly to form carbides and to increase the corrosion strength and balances the structure for applications in high temperatures is the chromium. With about 10%, eutectic carbides type M<sub>7</sub>C<sub>3</sub> are formed. For low concentrations, type M<sub>3</sub>C prevails. More significant yet is the effect that the high concentration chromium causes

during the solidification, by changing the matrix to a microstructure where the carbides type  $M_7C_3$  are surrounded by an austenitic matrix or products from its transformation. For low concentration chromium, the carbides type  $M_7C_3$  form the matrix. Because of its characteristics of solidification, hypoeutectic cast irons with type  $M_7C_3$  carbides are naturally more resistant and harder than those that contain type  $M_3C$  carbides. Due to the major part of chromium in cast irons be combined with carbon as carbides, it is less effective than molybdenum, nickel and manganese or copper, in the eutectoid to pearlite transformation, then it has a minor effect in the quenching properties, as for steel. Besides that, chromium is the element more effective to improve the resistance under high temperatures and for protection against oxidation. It stabilizes the iron carbide so it decreases the probability of its rupture under high temperatures. For temperatures over  $760^\circ\text{C}$  chromium at 5% rate grants to cast iron resistance to oxidation (ASM International, 1990).

The aim of the proposed work is to study the corrosion and worn-out properties in high-silicon cast iron alloys which contain chromium concentrations of 0.11% and 4.16%, for in ferrous alloys, generally speaking, a growing percentage of chromium increases the corrosion strength as a consequence of chrome-oxide formation and also the wear strength due to the chrome carbides. In this study specifically we seek to know whether the effects of chromium are the same in the presence of high amount of silicon (hydrated silicon oxide).

## 2. MATERIALS AND METHODS

Two different high-silicon cast iron alloys were used, tagged as A and B, whose the real chemical compositions are presented in Tab. 1. The process of making these alloys was presented by Castro et al in another scientific paper (Castro, 2006). It is observed the large existent difference between them regarding the chromium concentration.

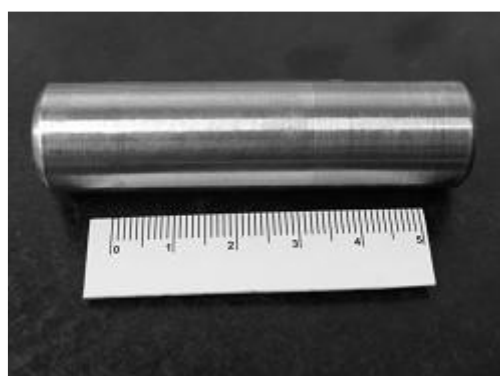
Table 1. Chemical composition of cast iron high silicon alloys (% in weight)

Chemical elements / Alloys	A	B
C	0.74	0,75
Si	14.43	14.46
Mn	0.43	0.42
P	0.015	0.015
S	0.012	0.011
Cu	0.44	0.43
Cr	0.11	4.16
Mo	0.35	0.34
Mg	0.020	0.005
Ti	0.174	0.021
Al	0.017	0.006
Ni	0.030	0.040

The wear/erosion trials were done in the Tribology Laboratory of Materials, Aeronautic and Automotive Engineering Department of Engineering School of São Carlos – USP, with an equipment built locally by the laboratory, presented in the Fig. 3(a). Figure 3(b) shows a milled sample.



(a)



(b)

Figure 3. Wear/Erosion trial (a) used equipment and (b) the milled sample

It has been observed the behavior under wear in five cylindrical samples, measuring 20 mm of diameter and 70 mm long, of each alloys (A and B), under abrasive/erosive environment. Firstly it was used a clay composed only by water

and aluminum and, later on, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> were added to clay. The composition of each out of four types of abrasive clay is showed on Tab. 2.

The specimens clamped to the revolving table were between centers in a distance of 110 mm. The tests were done at 1000 rpm during 1, 2, 3, 4 and 4 hours, resulting in a roamed distance of 21.113 m, 42.226 m, 63.340 m, 84.453 m and 105.567 m, respectively.

Table 2. Composition of the abrasive clays used during the tests

Clays	H <sub>2</sub> O distilled (mL)	Al <sub>2</sub> O <sub>3</sub> (mL)	H <sub>2</sub> SO <sub>4</sub> (mL)	HNO <sub>3</sub> (mL)
1	5000	1000	-	-
2	5000	1000	330	-
3	4850	1000	-	150
4	5000	1000	-	330

Tests of loss of mass by immersion were performed according to ASTM G-31 designation in alloys A and B, in the corrosives medium of H<sub>2</sub>SO<sub>4</sub> 20% and HNO<sub>3</sub> 65% at 92°C. Initially each specimen of 40 mm of diameter and 6 mm thick, as shown on Fig. 4(b) were cleaned with acetone and alcohol then dried in hot air. The tests were done in Erlenmeyer which contained at least 20 mL of solution per square centimeter of sample surface connected to a reflux condenser as seen on Fig. 4(b).

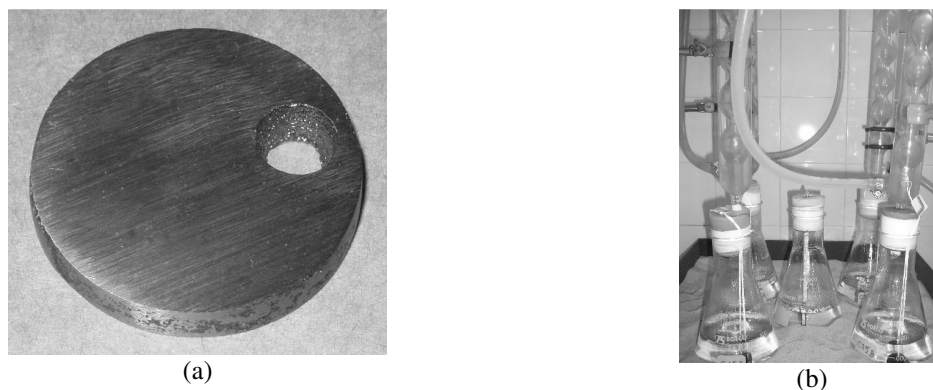


Figure 4. Corrosion tests (a) specimen used during testing sessions and (b) immersion testing system heated in sand at 92°C

Samples were removed from the corrosive medium then they were mechanically cleaned in order to remove the corrosion products. They were weighed in analytic scale. For the H<sub>2</sub>SO<sub>4</sub> solution, samples were assessed within 72 and 144 hours of immersion, using different specimens for each analyzed condition without test interruptions. In the HNO<sub>3</sub> solution, the assessments were done only with 144 hours of test. The results of loss of mass for short periods were ignored since the corrosion rate decreased along the time. For that reason, it was appropriate to calculate the corrosion rate from the loss of mass dimensions with low time of exposure.

The corrosion rates, measured in mpy (millesimal inches per year) were taken according to ASTM G-31 designation, through the Eq. (1), where  $W$  is the loss of mass in g,  $A$  is the exposed area in square centimeter,  $T$  is the time of exposition in h, and  $D$  is the specific mass of 7.0 g/cm<sup>3</sup>, according to ASTM G-1 designation,

$$mpy = \frac{3450000 * W}{A * T * D} \quad (1)$$

### 3. RESULTS AND DISCUSSIONS

The wear/erosion tests were performed to compare the performance of two high-silicon cast iron alloys under wear (A and B) hence these tests allow us to foresee the behavior of each sample under real working conditions. Figure 5 shows the specimens after test and clamped to the revolving table. It was observed loss of mass by the “rounding” of the top end of these specimens.

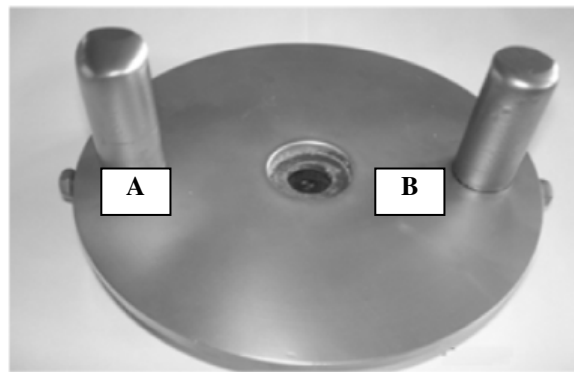


Figure 5. Featuring round table and the tested specimens

Figures from 6(b) to 6(d) present the loss of mass in the alloys A and B due to the time of exposition in clays from 1 to 4, respectively. It is observed that in clay 1 a very clear rate of loss of mass in A is higher than B. By the other hand in clay 2 it is observed in the bottom of the graphic that the loss of material A is about 3 times bigger than the material B. Regarding clay 3 it can be observed that the difference of loss of mass between materials A and B increased through the use of nitric acid, while the material A presented a loss of mass corresponding to 3.5 times bigger than the material B. Last, clay 4, with the increment of nitric acid, besides the difference between the loss of mass by materials A and B, such difference was lower than presented, compared to clay 3.

The increase of chromium level in the formation of a large amount of chromium carbides which increases the material hardness, consequently it increases the material strength to wear/erosion. It explains the behavior of alloy B related to alloy A facing the loss of mass in tested materials submitted to the wear/corrosion tests, since the last alloy presents chromium level smaller when compared to alloy B. Regarding to the resistance to erosion it is necessary to assess angles of incidence of particles in order to get the best implication to a more suitable material.

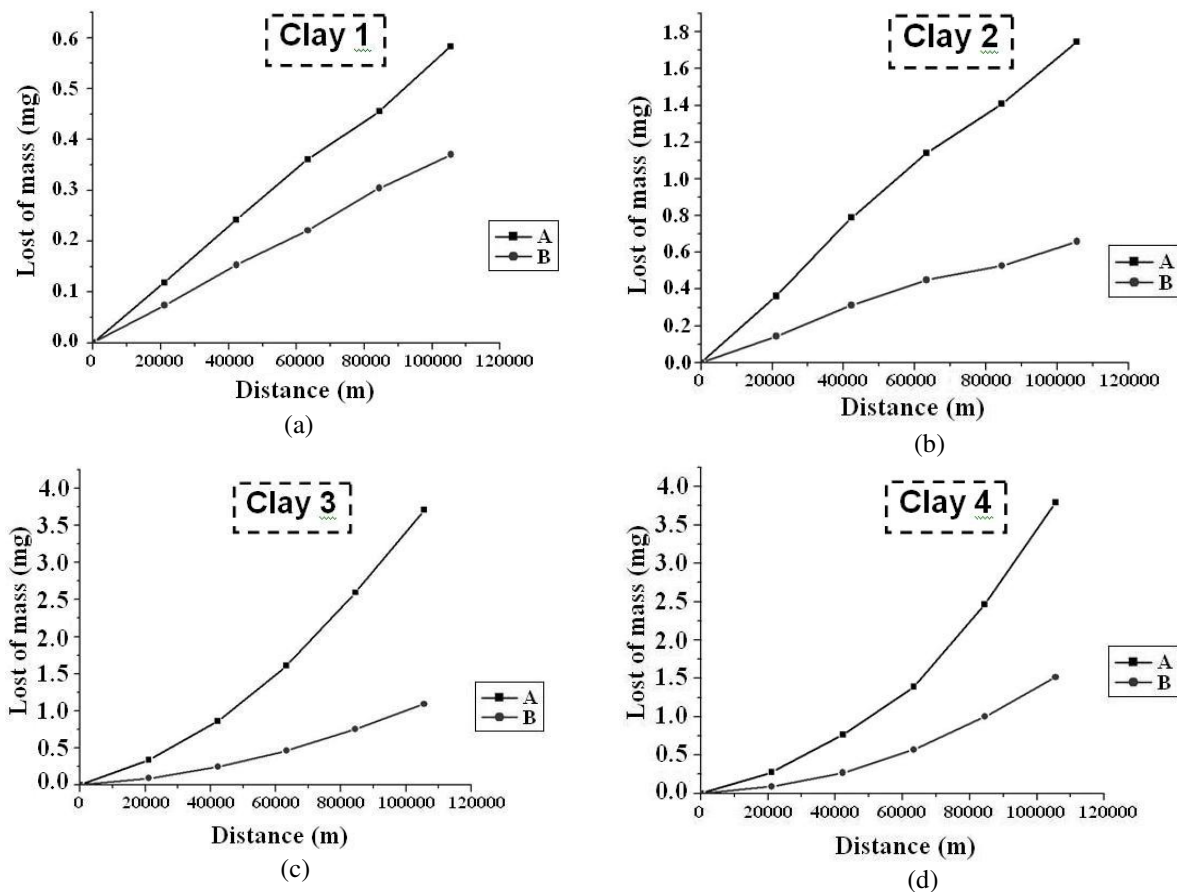


Figure 6. Loss of mass in test specimens of alloys A and B, due to the roamed distance in clays from 1 to 4 respectively

Figures 7(a) and 7(b) illustrate the loss of mass by corrosion due to the time, for alloys A and B immersed in  $H_2SO_4$  and  $HNO_3$  solution, respectively. It can be observed in image 7(b) that the corrosion strength of alloy B which was submitted to corrosion in sulfuric acid at 20% is superior than the alloy A. After 72 hours the obtained corrosion rate of B was 4.2 mpy which means that it was almost 20 times smaller than alloy A, 71 mpy. After 144 hours corrosion rates of 35 mpy were achieved for alloy A and 4.3 mpy for alloy B. Considering that the longer the corrosion tests is the more significant the achieved results are these last figures of corrosion are the ones that must be taken into consideration for analysis of corrosion strength in the studied materials.

Even though, according to Fig. 7(b), it can be observed that the two alloys present corrosion rates very low in nitric acid, that is, at the rate of  $10^{-1}$  mpy. Therefore, both materials present high corrosion strength in nitric acid 65% at 92°C. Alloy B presented smaller corrosion rate, which can be related to its higher chromium concentration. The corrosion rates of alloys A and B were 0.47 and 0.37 mpy, respectively. This way they comply with the rates provided by Fontana that varies within the interval of 0 to 5 mpy in nitric acid in the same concentration and temperature (Fontana, 1987).

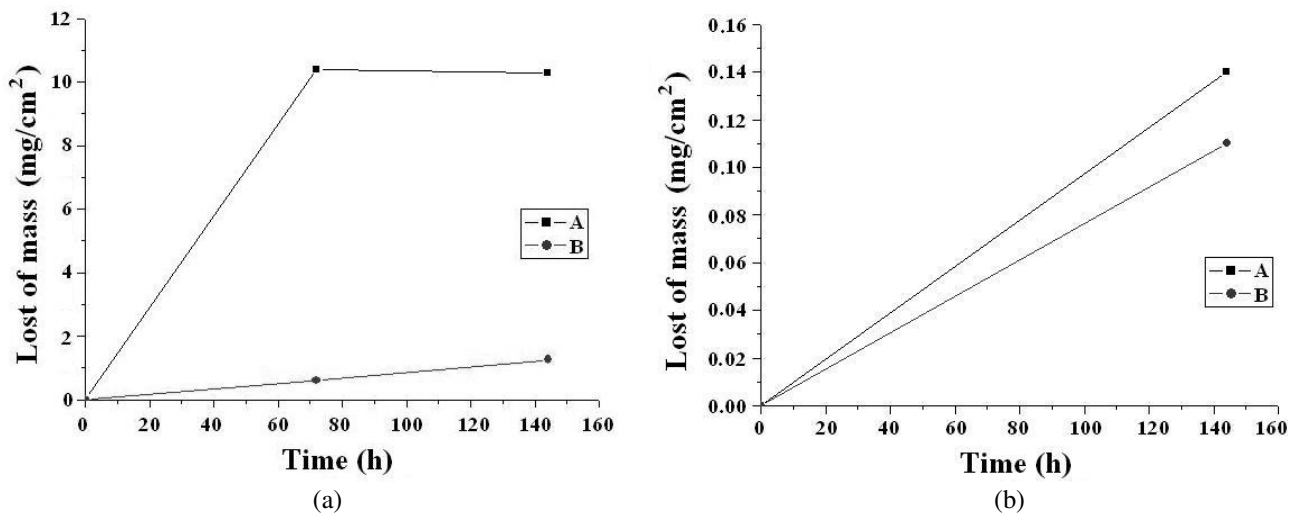


Figure 7. Average loss of mass of two samples of cast iron high silicon according to the immersion time at the temperature of 92°C in (a) sulfuric acid 20% and nitric acid 65%

As mentioned before, the high concentration of silicon in the alloys A and B promotes the formation of a protective coating of hydrated  $SiO_2$  in the material surface, which gives corrosion strength in these alloys. In the present study the higher corrosion strength in alloy B is due to the higher concentration of chromium in it. Despite of that the corrosion rates of alloy A that presented smaller resistance in the studied conditions are the same magnitude than the ones provided by Fontana for Duriron in  $H_2SO_4$  20% at 92°C (5-20 mpy) (Fontana, 1987). Figure 8 shows data about corrosion in some alloys of nickel in sulfuric acid, through a diagram where regions are defined due to temperature and sulfuric acid concentration and corrosion rates of alloys are smaller than 20 mpy (Hurst, 1943). It is observed that the corrosion rate of A, despite of being higher than B, it is compared to the Monel super alloy in sulfuric acid.

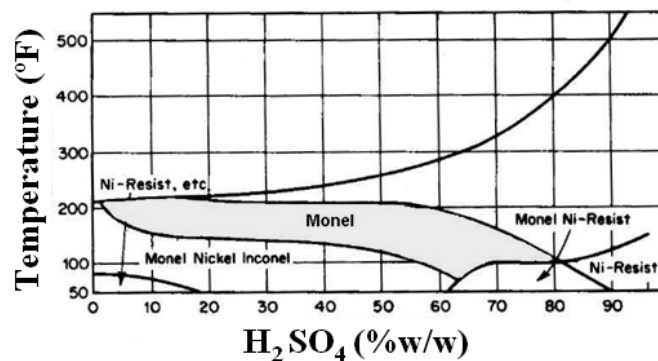


Figure 8. Regions with corrosion rates of 20 mpy or smaller for several alloys of nickel in sulfuric acid according to concentration and temperature (Hurst, 1943)

Figures 9 and 10 present the superficial aspects of samples respectively after the immersion time in  $H_2SO_4$  20% and  $HNO_3$  65% at 92°C. Figure 9 it is evident the smallest corrosion strength of sample B, that presents shiny surface in

both immersion times. Figure 10 it is noticeable the shiny superficial aspect in both alloys in the immersion time of 144 hours. It can be related to a capacity of chromium to form a passive layer in the material surface, forming a fine and adherent oxide film, which works as a protective layer against additional corrosion. If damaged, the protective film usually regenerates very quickly. (Ashby, 2007; Callister, 2006).

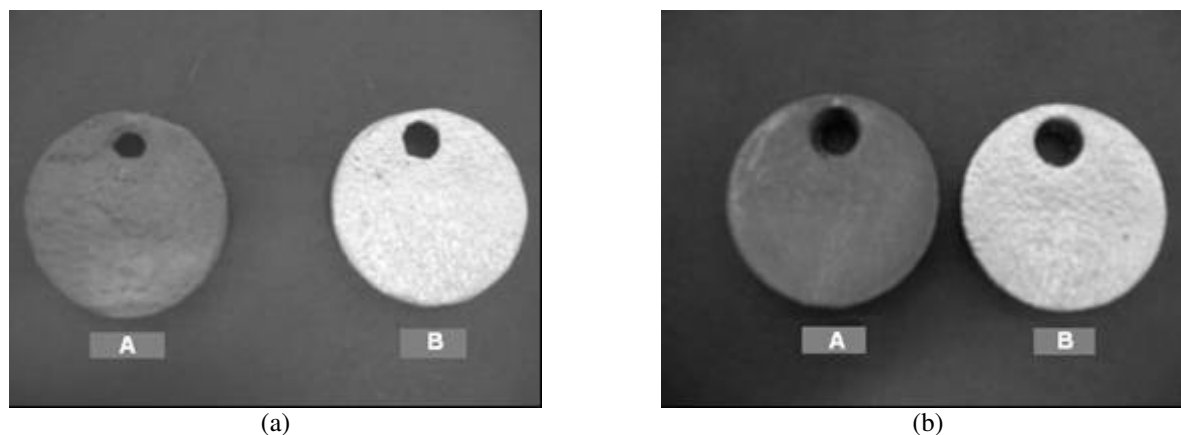


Figure 9. Sample aspects after (a) 72 hours and (b) 144 hours of immersion in  $H_2SO_4$  20%, at  $92^\circ C$

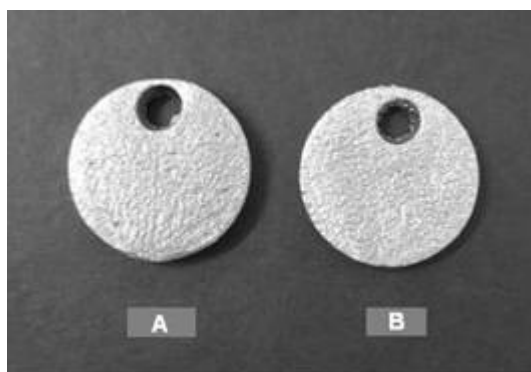


Figure 10. Sample aspects after (a) 144 hours of immersion in  $HNO_3$  65%, at  $92^\circ C$

#### 4. CONCLUSIONS

The wear strength of alloy B was superior than alloy A under any test conditions, distinctly due to the higher level of chromium. Alloy B also presented a slightly better behavior under corrosion than alloy A in all tests.

It is important to mention, though, besides that alloy A was less resistant than alloy B, it was still effective corrosion strength as a cast nickel super alloy, M 35.1 (Monel 400), whose final cost is twenty times more expensive if compared to alloy A studied in this paper. Thus, alloy A can be recommended for use in less aggressive medium since its low level of chromium, it presents a cost of production smaller than alloy B.

#### 5. ACKNOWLEDGEMENTS

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