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Short communication

# Effect of boronizing composition on boride layer of boronized GGG-60 ductile cast iron

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ABSTRACT

Boronizing of GGG-60 nodular cast iron samples were performed by immersion in molten salts. These were based on borax containing eight reducing agents: $Na_2CO_3$, $CaCl_2$, NaCl, NaOH, $B_4C$, SiC, Al and ferrosilicon. Also the cast iron samples were boronized with pack boronizing method using different mixture compositions such as $B_4C$, borax, $Na_2CO_3$, and SiC. This work gives a survey on the nature and quality of the layers which were obtained according to the boronizing composition. The effects of the boronizing bath composition on the obtained layers' quality are also discussed. The results of the studies show that the most suitable boronizing compositions for electroless liquid boronizing of GGG-60 cast iron are %65 borax – 25% Fe–Si – 10% NaOH and 70% borax – 30% $B_4C$ in order to obtain the hardest and the thickest boride layer. On the other hand, the suggestible composition for pack boronizing of it is 85% $B_4C$ – 15% $Na_2CO_3$.

Ductile iron, also known as ductile cast iron, is a type of cast iron. While most varieties of cast iron are brittle, ductile iron has much more impact and fatigue resistance, due to its nodular graphite inclusions [1]. Boronizing is a thermochemical surface treatment that can be applied to a large range of materials (ferrous metals, non-ferrous metals and cermets). As is the case for other thermochemical surface treatments, boronizing can be achieved in all environments by various processes and techniques:

- in a solid environment using powders or pastes [2–6].
- in a liquid environment of molten salts with or without electrolysis [7–12].
- in gaseous surroundings [13,14].

Boronizing works by introducing boron atoms by diffusion into a substrate surface. The introduced boron atoms react with the material and form a number of borides. Diffusing boron into the iron crystalline lattice leads to the formation of two kinds of iron borides (FeB and $Fe_2B$) [15]. Also to improve wear resistance, boronizing enhances also the corrosion resistance and oxidation resistance at temperatures of up to 850 °C. The main disadvantage of boronizing is the brittleness of the compound layer, especially the FeB phase [16]. Growth and phase composition of the boride layer can be influenced by the alloying elements in the base material. The microhardness of the borided layer also depends strongly on the composition and structure of the boride layer and the composition of the base material. Also various investigations show that boriding agents and their compositions in boronizing medium are very effective on the formation of boride layer and phases.

The main objective of this study was to investigate the effect of boriding agents and their compositions in boronizing medium on the formation and morphology of boride layer in ductile cast iron (GGG 60) at constant boronizing time and temperature. Each sample was studied by performing micro-hardness measurements, optical microscopy, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis. The phase identification of the treated samples was made by X-ray diffractions using $K_{\alpha 1}$ Copper line ($\lambda_{K\alpha 1}$ (Cu) = 1.54 nm).

Ductile cast iron samples of 10 × 10 × 10 mm were machined from GGG-60 ductile cast iron which was produced in ESTAS camshaft foundry. The weight percent chemical composition of the GGG-60 ductile cast iron was determined by spectrometry as %3.70C, %1.82 Si, %0.66 Mn, %0.45 Cu, %0.43 Mo, %0.40 Cr, %0.24 Ni, and balance Fe. Just before boronizing, all samples underwent a surface preparation with silicon carbide abrasive to eliminate all contamination that can hinder boron diffusion through the surface.

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Boronizing treatment was carried out in two different mediums, which one of them was a liquid medium (salt bath) (M1-M13 Table 1) the other one was a solid medium (M14-M18 Table 1). It was performed by putting the study samples and the chemical agents (Table 1) into a sealed ceramic crucible, which was then heated in an electrical resistance furnace. All of the mixtures of boronizing agents were prepared as 20 g. Boronizing time and temperature were kept constant as 4 h and 950 °C, respectively. After boronizing, the samples were cooled in a furnace and then cleaned in hot water. Boronized samples were sectioned and ground using 1200 grid emery paper and then polished by alumina paste. Polished samples were etched with Nital ($HNO_3$ 3%).

Some of the cross-sectional microstructures of the boronized different specimens are shown in Fig. 1. It can be seen that borides (FeB and $Fe_2B$) or boride layers are not formed on the substrate surfaces of some of the specimens. It means that some of the suggested boronizing compositions in the literature are not suitable for boronizing of GGG-60 ductile cast iron. Especially when microstructure photograph and hardness distribution of layers of M5, M9, M10 and M11 coded experiments in Fig. 1 and Table 1 are examined; it shows that boride layers aren't occurred on the surface of the samples. So compositions (wt. %) of boronizing mixtures in these experiments are not suitable for boronizing of GGG-60. Melting temperature low salts (NaCl, CaCl, NaOH, and $Na_2CO_3$) were added to these mixtures as shown in Table 1 in order to decrease the viscosity of salt bath, so diffusion of boron into substrate would be easier. But this theory was not successful as seen in microstructure photograph of M5 and M9 in Fig. 1. According to Lyakhovich et al. [17], electroless liquid boronizing in molten salts is obtained from the formation of a galvanic cell. The spatial separation of the redox process into a cathodic and anodic stage is possible only when there is an electrochemical difference between the treated metal and the particles of the reducing agent and when there is an electrical contact between them. For the cathodic process to take place on the surface of the metal being saturated, its electrode potential must in specified conditions (composition of electrolyte, temperature) be positive and higher than the potential of the reducing agent. The electrode potential of the cathodic process to take place on the surface of the metal being saturated might be negative and lower than the potential of the reducing agent in M5, M9, M10 and M11 mixtures, therefore bored layers were not formed on the surface of the specimens. This situation is confirmed by the X-ray diffraction pattern of M10 in the Fig. 3. Bored layers might be occurred by Electrolytic Liquid Boriding method in these mixtures.

A medium level thick boride layer was obtained by using Fe–Si as a reducing reagent in mixture M1, M3 and M4. Effect of Fe–Si on boride layer appears obviously in M1's microstructure photograph in Fig. 1. When we compare the microhardness of M1, M3 and M4 (used Fe–Si in mixture) with M5, M9, M10 and M11 (not used Fe–Si in mixture) in Table 1, this result gets over that a reducing reagent like Fe–Si must be added to boronizing mixture bath for electroless liquid boriding of GGG-60 ductile cast iron. Because, according to Lyakhovich et al. [17], on borating with B, Al, calcium-silicon, Mn, Si, Ti, $B_4C$, FeB and $Fe_2B$ phases are formed on the iron, since the potentials of them are more negative than those of boride phases. Addition of sodium hydroxide to electroless liquid boronizing mixture cause the formation of the thickest and hard boride layer formation on the surface of GGG-60 ductile cast iron as shown its microstructure photograph (M2) in Fig. 1 and Table 1. Also the result of X-ray diffraction analysis of the M2 in Fig. 3 show that the borides which were formed by using sodium hydroxide. The reason of this situation might be low melting temperature of NaOH. NaOH in mixture M2 decreases the viscosity of the salt bath, so diffusion of reduced boron in bath increase, therefore the formation of borides might be easy and fast. As a result, using of NaOH as a diluent instead of $Na_2CO_3$, NaCl, CaCl and $B_2O_3$ might be preferential for electroless liquid boronizing of GGG-60 ductile cast iron.

In the case of the borax–$B_4C$ mixture (M6), the formation of thick and hard boride layer (Table 1, the hardness distribution of the boride layers) can be explained by the very boron-rich bath. The formation of moderate hard boride layer (Table 1, hardness distribution of M8) by using borax–SiC mixture can be explained by the fact that the potential difference between the treated piece and the suspended micro-anodes SiC does not ensure a sufficient boron flux for the formation of a boron-rich boride layer. A similar hardness distribution in M8 is obtained by M12 mixture, the reason of that composition of M8 and M12 is very similar to each other. It is expected that the hardest boride layer formation is occurred by using the borax-Al bath (mixture M7), because according to Ellingham's diagrams, the reduction of boron oxide resulting from the thermal dissociation of borax, is made easier by aluminum than carbon or silicon. However, this fact was not occurred in our study as shown in the hardness distribution of M7 in Table 1. As a result, using of the borax–$B_4C$ mixture (M6) as a salt bath causes the thick and hard boride layer formation on the surface of GGG-60 ductile cast iron.

**Table 1**
Compositions (wt.%) of boronizing mixtures and the microhardness ($HV_{0.5}$) distribution of boride layers of the electroless liquid and pack boronized ductile irons from surface to interior after boronizing for 4 h.

| Mixture | Compositions, (wt.%) | | | Microhardness ($HV_{0.5}$) distance from the surface | | | |
|---|---|---|---|---|---|---|---|
| | | | | 40 μm | 80 μm | 120 μm | 160 μm |
| M1 | Borax, 65 | Fe–Si, 25 | $Na_2CO_3$, 10 | 967 | 920 | 852 | 601 |
| M2 | Borax, 65 | Fe–Si, 25 | NaOH, 10 | 1402 | 1203 | 1170 | 979 |
| M3 | Borax, 65 | Fe–Si, 25 | $B_2O_3$, 10 | 832 | 705 | 669 | 522 |
| M4 | Borax, 65 | Fe–Si, 25 | $CaCl_2$, 10 | 783 | 649 | 542 | 526 |
| M5 | Borax, 65 | NaOH, 25 | $B_2O_3$, 10 | 335 | 323 | 250 | 200 |
| M6 | Borax, 70 | $B_4C$, 30 | | 1307 | 1166 | 1083 | 961 |
| M7 | Borax, 70 | Al, 30 | | 500 | 473 | 351 | 330 |
| M8 | Borax, 70 | SiC, 30 | | 804 | 746 | 613 | 549 |
| M9 | Borax, 65 | $Na_2CO_3$, 10 | NaCl, 25 | 306 | 301 | 297 | 250 |
| M10 | Borax, 65 | $CaCl_2$, 10 | NaCl, 25 | 311 | 308 | 294 | 268 |
| M11 | Borax, 90 | $Na_2CO_3$, 10 | | 330 | 310 | 243 | 224 |
| M12 | Borax, 73 | SiC, 24 | NaCl, 3 | 765 | 617 | 564 | 441 |
| M13 | NaOH, 85 | $B_2O_3$, 15 | | 424 | 374 | 355 | 263 |
| M14 | $B_4C$, 85 | $Na_2CO_3$, 15 | | 892 | 855 | 814 | 787 |
| M15 | $B_4C$, 95 | Borax, 5 | | 420 | 270 | 291 | 234 |
| M16 | $B_4C$, 85 | NaOH, 15 | | 552 | 504 | 458 | 400 |
| M17 | SiC, 85 | $B_2O_3$, 15 | | 406 | 404 | 392 | 310 |
| M18 | $B_4C$, 95 | NaCl, 5 | | 502 | 439 | 342 | 287 |