Microstructural Characteristics of Electric Discharge Alloyed Layers on Spheroidal Graphite Cast Iron with Different Electrode Materials

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In this study, electrical discharge alloying (EDA) is used to modify the surface of ferritic spheroidal graphite cast iron. Under the conditions of fixed EDA parameters and variable elements (i.e., electrode materials Fe–75 mass% Si, Al, Ni, Mg and Cr), these alloying elements are dissolved in substrate. Then, the effects of alloying with different alloying elements on the EDAed layers are investigated. Experimental results reveal that the Mg electrode has produced the thickest EDAed layer while the Cr electrode has produced a thinner layer. Additionally, EPMA/mapping is also used to analyze the distribution of different elements in their respective EDAed layers and X-ray diffraction is used to analyze the phase compositions of these layers. The results of hardness tests reveal that the EDAed layer with Cr has the highest hardness value. This may be related to the formation of carbides that contain Cr in the layer.

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1. Introduction

Ferritic spheroidal graphite (SG) cast iron has become an extensively used industrial material for its numerous excellent qualities such as good castability, ease of machining, low cost.²,³ Its mechanical properties such as strength, hardness and ductility can also be varied by controlling its matrix and chemical composition. Because of the extensive and frequent use of this material, workpieces made of it often encounter problems such as corrosion, wear and high-temperature oxidation on the surface in many applications.⁵ After long-term use, their precision is likely to decline, thereby shortening their life cycles. Therefore, many researchers share the common goal of finding a method of surface modification that increases the durability of work pieces without losing the intrinsic properties of the material.⁴–²⁵ In order to increase the applications of SG cast iron, a simple and rapid surface modification technique that boosts the resistance of the material surface against corrosion, wear and high temperature oxidation must be developed.

Cooling rates and the addition of alloying elements are the main factors that dominate the solidified structures of SG cast iron, which in turn affect its various mechanical properties.²⁶,²⁷ Therefore, the main method of improving mechanical properties of SG cast iron is to change cooling rates and add alloying elements. An increase in the silicon content in SG cast iron has several merits, including increasing the $A_1$ temperature of austenitizing transformation, facilitating graphite formation, enhancing strength, increasing the resistance against high temperature oxidation, and reducing hysteresis loss. Moreover, silicon is a ferrite-promoting element that has an effect of solid solution strengthening on the ferritic phase.²³ Higher tensile strength, better resistance to thermal shock, high graphitising tendency, good scaling resistance at high temperature and good machinability are some of the advantages which are obtained by adding aluminum to cast irons. The satisfactory strength of Al-alloyed ductile irons provides the potential of this low-alloy ductile iron for elevated temperature service.²⁹ Chromium is a carbide-promoting element in SG cast iron and one of the pearlite-promoting elements. It contributes to the formation of carbides that contain Cr, which increases wear resistance, in SG cast iron that is used for anti-oxidation and anti-corrosion.³⁰ Nickel is an austenite-stabilizing element that can reduce the temperature of $\gamma - \alpha$ transformation, promote the stabilization of austenitic matrices. It bestows a capability of solid solution strengthening in ferrite. Each addition of 1% nickel allows an increase in the hardness of ferrite by 15HB and an increase in yield strength by approximately 40 MPa.³¹ When the magnesium will be added to the molten cast iron as desulfurizing agent and deoxidizing agent, changing the graphite morphology and promotes the formation of carbides.¹,³ In summary, these alloy elements, when added into SG cast iron, all act to promote its hardness and resistance against wear and corrosion. In consideration of the fact that any increase in cooling rates are limited by the size of work pieces and external environments, the only feasible method is promoting the properties of SG cast iron by adding alloying elements. Electrical Discharge Alloying (EDA) is a new process that uses an electrical discharge machine to perform surface modification of work pieces.²⁵ The electric arc discharge between the electrode and the base material can melt both. The molten electrode material is then transferred to and reacts with the surface of the base material. The base material thus undergoes surface alloying. Mohri et al.⁵ carried out surface modification on workpieces of carbon steel and aluminum using composite electrodes of copper, aluminum, tungsten carbide and titanium in hydrocarbon oil. The existence of electrode materials in the surface layers of workpieces significantly changes the characteristics of these layers. The EDA modified layer, which is obtained

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relatively rapid, possesses sufficient engineering thickness and hardness. The process characteristically brings about structures that have higher solidification rates and modified layers with alloying elements. Therefore, it is used herein to modify the surface of ferritic SG cast iron. The purpose is to obtain surface-modified layers that contain different alloying elements using different alloy electrodes. The structures and characteristics of the alloyed surface-modified layers are further examined in order to provide references and bases for the process of modifying the surface of SG cast iron using EDA.

2. Experiment Procedure

2.1 Specimen preparation

The specimens (ferritic SG cast iron) that were used herein were prepared as follows. The specimens were obtained by melting pig iron, silicon steel and ferrosilicon in a high frequency furnace, and these materials were used to regulate the carbon and silicon contents in the specimens. The materials were melted into molten liquid in the furnace until the liquid reached the intended temperature before it was poured into an inoculant and a spheroidizer for inoculation and spheroidization. It was then poured into a Y-shaped sand mold with the dimension of 150 mm × 100 mm × 30 mm in the parallel section and air cooled to room temperature. All the specimens underwent a two-stage ferritization treatment. In the first stage, the specimens were heated at a constant temperature of 1203 K for three hours and, furnace-cooled to at a constant temperature of 1003 K for five hours in the second stage, and eventually to room temperature. The ferritized specimens were milled to the dimensions, as shown in Fig. 1. Their milled surfaces were ground using a 600 grit paper to maintain uniform surface roughness. Figure 2 presents the metallurgical structure of ferritic SG cast iron. Table 1 depicts its chemical composition (3.4 mass% C, 3.2 mass% Si), as revealed by spectral analysis.

2.2 Electrical discharge alloying process

The process was used to study the alloyed layers that were formed by the rapid solidification of residual molten materials, which took place due to the rapid cooling of the dielectric fluid following electrical discharge machining (EDM). Figure 3 schematically presents the EDA process. Table 2 lists the electrical discharge conditions for the Fe–75 mass% Si electrode and other different electrode materials.
alloyed layers. This helped the subsequent analysis of microstructural characteristics of the alloyed layers in this study. These alloyed layers also have fewer defects (e.g., micro-cracks or pores) in the solidified structures and more appropriate thickness and therefore can better meet the needs of actual application. Experiments herein were conducted using continuous electrical discharge and force sludge in order to reduce the carbon effect.

2.3 Microstructure observation and composition analysis

After the EDA modified specimens had undergone grinding, polishing and etching using a 5% nital etchant, their microstructure of EDAed layer were observed using an optical microscope. The microstructures of the alloyed layers were also observed using SEM after the layers had been etched using a HNO₃, HF and glycerol solution. To examine the alloying extent and the compositional distribution of the modified layers, SEM and EPMA/mapping were used to conduct a composition analysis of the cross-sections of the non-etched layers. X-ray diffraction was also used herein to analyze and identify the crystallographic structures of solidified layers and compare structural differences between base metal and modified layers. The crystallographic structure of the modified layers was determined by glancing angle X-ray diffraction (GAXRD) at a glancing angle of 3° using Cu Kα₁ (0.15405 nm) radiation.

2.4 Hardness testing and thickness measurement on EDA modified layers

To examine the effect of electrode materials on the hardness of the EDAed layers, Vickers microhardness testing machine was used to test the cross-sections of the polished specimens. The testing conditions were a 50 g load, applied for 20 s. All of the results of hardness testing were the mean values of five point data. Following 5% nital etching, thickness measurement was conducted on the EDA-treated specimens using SEM at the fixed magnification of 500× to obtain the mean values of thickness of the 15 alloyed layers that were measured.

3. Results and Discussion

3.1 Microstructural observation of EDAed layers

Upon the formation of electrical discharge arc, the surfaces of the machined sections are quickly heated to 8000–12000°C or 20000°C and then rapidly cooled. The remaining superficial layers on the machined sections were thus modified and exhibited properties that differed from those of the base metals. Figure 4 presents the SEM topographical surface images of the alloyed layers as well as their post-etching SEM cross-sectional microstructures. It reveals that the surface defects of the EDAed specimens include re-melted solidified structures, craters, pores and cracks etc. (Fig. 4(a)). There is also a clear interface between the rapidly solidified base metal and the as-machined layer, as shown in Fig. 4(b). The findings of observation, as shown in Fig. 4(b), further reveal the presence of cracks in the EDAed specimens. The cracks are formed by the tensile stress in the EDAed specimens that is caused by melting and cooling in a short time. Cross-sections of the EDAed specimens were obtained and deeply etched using an etchant to observe the microstructures of the specimens, including the base metal, the interface regions and the EDAed layers using SEM. Figure 5 presents the findings of observation. According to Fig. 5(c), SEM at a higher magnification reveals the presence of tiny graphite particles in the EDAed layers. These are the graphite residues that remain because a part of the base metal is not fully melted and scattered by the discharge sparks and the dielectric fluid is thermally decomposed. Another cause to this occurrence is that tiny graphite particles are crystallized because the EDAed layers have a fairly high carbon content (3.5–6.9 mass%) and the impurities in the dielectric fluid may become the nucleation sites for the formation of graphite.

3.2 Hardness and thickness comparison between alloyed layers created with different electrode materials

The alloyed layers were tested herein to investigate the effect of EDA electrode materials on their hardness. Figure 6 presents the results of thickness tests on the alloyed layers and reveals that is formed with an Mg electrode is the thickest while the same that is formed with a Cr electrode is the thinnest. The main factors that affect the thickness of alloyed layers are the nature of tool electrodes and the parameters of the EDA process. Some researchers point out that the melting point, thermal and electric conductivity of the electrodes all affect the thickness. Wang et al. examined the mechanism with which the EDM process was employed to form strengthening layers in the surface of stainless steel and the main factors that affected this mechanism. Their findings reveal that the...
The melting point of tool electrodes is a more important factor. The fact that electrodes with low melting points can increase the tool electrode wear rate in the EDA process, thereby reducing the workpiece materials removal rate contributes to the transfer of tool electrodes to the surfaces of workpieces, thereby increasing the thickness of alloyed layers. Higher thermal and electric conductivity also contributes to an increase in the thickness. Furthermore, the findings of many studies indicate that increased discharge current and pulse duration also lead to increase thickness. Figure 7 presents the hardness comparison between the alloyed layers that are with different electrode materials (Si, Ni, Cr, Al and Mg). The approximate hardness values of the alloyed layers that are formed with these different electrode materials are as follows: Hv 1120 with Si, Hv 760 with Al, Hv 1280 with Cr, Hv 930 with Ni, and Hv 910 with Mg. The results reveal that these different electrode materials have all contributed to higher surface hardness of SG cast iron. The alloyed layers of SG cast iron following the EDA process experience significant increases in hardness mainly because of micro-structural refinement caused by rapid solidification, solid solution strengthening (Si, Al and Ni element) and precipitation strengthening.

3.3 Composition distribution of element and phase analysis on surface modified layers with different alloy elements

Figures 8 to 12 presents the results of EPMA/mapping analysis of these different alloyed layers. Among the elements, Cr, Ni and Al have notably dissolved in the alloyed layers, thereby contributing to the higher hardness of these layers. On the other hand, the alloyed layer that is formed with Mg has many crystallized tiny graphite particles, as shown in Fig. 12, because Mg is a spheroidizing element for SG cast iron. The X-ray diffraction result also reveals that
the crystallographic structure of the base metal, SG cast iron, is α-Fe phase. Yang et al.\textsuperscript{35–37} examined the rapidly solidified structures of the cast iron alloy, Fe-1.77\textsuperscript{3}3.60 mass\%C-2.23\textsuperscript{12.06 mass\%Si}. Their findings reveal the presence of α, α', γ, Fe₃C phases and a metastable phase, which is usually called χ(Chi)-phase and has a complex BCC crystal structure of the α-Mn A12 type. The silicon element in the alloy can suppress the formation of martensite, retain the ferrite phase, and promote the formation of a new metastable χ(Chi) phase. By comparing the JCPDS X-ray diffraction files (No. 26-1141 and No. 47-1293) and Yang et al.'s studies, we infer the possible presence of χ(Chi) and Fe₂Si phases in the silicon alloyed layer, as shown in
Moreover, Fig. 13(b) presents the X-ray diffraction patterns of the alloyed layer that is formed using an Al electrode. We infer the possible presence of AlFe$_3$C$_{0.69}$ and FeC phases (JCPDS X-ray diffraction files No. 3-965 and No. 6-686). The alloyed layer that is formed using an Al electrode may contain AlFe$_3$C$_{0.69}$ and FeC phases, partly because Al is an element that suppresses the formation of nodular graphite. The AlFe$_3$C$_{0.69}$ phase is a nonequilibrium phase structure of ordered FCC and has excellent anti-corrosion resistance and greater hardness.38) On the other hand, Fig. 13(c) presents the X-ray diffraction patterns of the alloyed layer that is formed using a Ni electrode, which show that the layer may contain (Fe,Ni) and Ni$_3$C phases (JCPDS X-ray diffraction files No. 47-1417 and No. 4-853). The analysis results of Morra et al.39) reveal that the (Fe,Ni) phase is a FCC structure and called £ phase. At a cooling rate of $10^5$–$10^7$ K/s, the solute carbon in the metastable nickel solid solution can reach a maximum solubility limit of 7.4 at%. Under the foregoing conditions and increased pressure, the metastable Ni$_3$C phase with a hexagonal structure may be obtained.40) Additionally, by comparing the JCPDS X-ray diffraction files (No. 65-897 and No. 6-687), we infer the possible presence of Cr$_7$C$_3$ and Cr$_3$C$_2$ phases in the chromium alloyed layer, as shown in Fig. 13(d). The presence of these two Cr-containing carbides contributes significantly to the increased hardness of the alloyed layers. In addition, Ruth and Cohen41,42) studied Fe-C alloys using the rapid solidification method and discovered a metastable phase, which has a HCP structure and has been designated as $\varepsilon$ (C$_{0.17}$Fe$_{0.81}$Si$_{0.02}$), but appears to be different from the well-known $\varepsilon$ carbide. By comparing the JCPDS X-ray diffraction files (No. 19-628 and No. 3-989) and Ruth and Cohen findings, we infer the possible presence of $\varepsilon$ and Fe$_3$C phases, as shown in Fig. 13(e), in the alloyed layer that is formed using a Mg electrode.

4. Conclusion

(1) The microstructures of the EDAed layers all comprise tiny dendritic crystals and have many tiny graphite particles.

(2) The effect of alloying using different electrode materials on the alloyed layers is investigated using fixed machining parameters. The experiment results reveal that the alloyed layer that is formed with the Mg electrode is the thickest while the same that is formed with the Cr electrode is the thinnest, but has the highest hardness value, which may be related to the formation of carbides that contain Cr in the layer.

(3) EPMA composition analysis presents that the contents of different alloying elements in the alloyed layers decrease as the distance from the electrical discharge end increases. However, performing EDA using Si, Al, Cr, Ni and Mg electrodes is feasible.
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