Microstructure analysis of surface coating of graphene modified Cr12MoV die steel by induction cladding

Liu Heping\textsuperscript{1,2}, Cheng Shaolei \textsuperscript{1}, Liu Langlang\textsuperscript{1}, Sun Fenger\textsuperscript{1}

1 School of Materials Science and Engineering, North University of China, Taiyuan 030051, China
2 Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada

E-mail: peace666@126.com

Abstract In this work, 316 stainless steel powder was used as base powder and graphene was selected as reinforcer. A stainless steel graphene composite coating was successfully prepared by induction cladding on the surface of cold working die steel Cr12MoV. The effects of different coating processes on the microstructure of the coating were investigated by metallographic microscope and scanning electron microscopy. The experimental results show that the bond strength of the coating and the mold steel substrate is perfect. No significant oxides are present in the grain boundaries. With the raise of induced current, the surface hardness of the composite coating increases gradually. In addition, with the increase of graphene content, the surface hardness of the coating also shows the same upward trend.

1. Introduction
The structure of graphene is a planar hexagonal honeycomb composed of a layer of carbon atoms, which has strong corrosion resistance. The corrosion resistance and wear resistance of metals can be improved by using graphene as metal protective layer. Graphene is one of the materials with the highest known strength. It also has good toughness and flexibility. The theoretical Young's modulus of graphene is 1.0 TPa and the intrinsic tensile strength is 130 GPa. Graphene is also increasingly used in surface strengthening of steel materials [1,2].

Generally speaking, wear, corrosion and fracture are the three main forms of material failure. The direct and indirect economic losses caused by corrosion, fracture and wear account for about 4% of the world's annual average GDP. The surface strength and corrosion resistance of steel are always contradictory. At present, the high strength steel materials used are generally high carbon steel. But it also brings an unavoidable problem, that is, the corrosion resistance of steel. But with the discovery of graphene, this contradiction has been well resolved.

Mold is the main processing tool for manufacturing industrial components. The quality of die steel directly affects the quality of pressure processing technology, precision production and production cost of products. The main series of cold-rolled die steel is high hardness and cold work, which is mainly used for dies requiring high compression resistance and wear resistance. The Cr12MoV used in the present work is a cold working die steel, which can reduce the carbon content of high carbon Cr12 steel. Cr12MoV is mainly used to manufacture various dies and tools with large cross-section, complex shape and heavy working load [3-5].
In this paper, a 316L/graphene composite coating was added on the surface of Cr12MoV die steel by induction cladding. The purpose of improving corrosion resistance and surface strength of die steel surface is realized, and the service life and application field of die steel are improved.

2. Experimental

2.1 Matrix Treatment
The Cr12MoV was chosen as the matrix material in the experiment. The die steel is cut into small discs with a diameter of 20 mm and a thickness of 3 mm. Before induction cladding, the two sides of die steel were polished with 600-1200 mesh sandpaper to remove the oxide on the surface of die steel. This is conducive to the adhesion of the coating material to the surface of the sample and to the enhancement of the bonding strength after cladding.

2.2 Mixing of Coated Powder Materials
In this work, the mixed powder of graphene and 316L stainless steel was used as coating material. The mass fractions of graphene were 0.2%, 0.3%, 0.4% and 0.5% respectively. In order to make the mixture of graphene and stainless steel powder uniform, dry ball milling was used in the experiment. The rotational speed of the ball mill is 200 r/min, the milling time 2 h, and the ball-to-material ratio 10:1.

2.3 Induction Cladding
The powder is coated on the surface of the sample which has been pretreated separately and compacted to make the surface smooth. Then the coated sample is placed in the coil of the induction cladding instrument. The high frequency induction heater is produced by Zhengzhou Kechuang Electronics Co., Ltd. The inverted frequency is 20-60 KHz, and the maximum heating current is 630 A. The induction heating current used in the experiment is 360 A, and the induction heating time is 20 s. The effects of different induction heating currents on the properties of the coating were also studied. The induction heating currents were 280 A, 320 A, 360 A and 400 A, respectively. The surface of die steel was pretreated before induction heating, and the thickness of powder laying was 0.5-1 mm.

2.4 Detection
The morphology and structure of the samples before and after electrochemical measurement were characterized by scanning electron microscopy (SEM, SU-5000), metallographic microscope (MDS 400). The surface hardness of the samples was tested by micro Vickers hardness tester (HVS-1000A).

3. Results and Discussion

3.1 Effect of different graphene content on cladding layer

![Figure 1. Surface morphology of cladding layer with different graphene content](image)

(a) 0.2%  (b)0.3%  (c) 0.4%  (d) 0.5%
In Figure 1, the cladding effect is good at different graphene content, and there are no large pore and particulate matter on the surface of the cladding layer. Figure 1 (a) and (b) have almost the same effect as the cladding layer, but the void content in Figure 1 (b) decreases and the surface becomes smoother. When the content of graphene reaches 0.4%, the surface properties of the cladding layer are the best, and no obvious voids are produced. However, with the increase of graphene content, many small holes appear in Figure 1 (d), and the smoothness of the cladding layer surface decreases. With the increase of graphene content, graphene exists at the grain boundary of the cladding layer. When the content of graphene is small, it has little effect on the cladding layer. However, as the content increases, graphene increases the risk of oxidation of grain boundaries at high temperatures, resulting in a large number of carbides and oxides at the grain boundaries. As a result, a small number of micro-pores appear on the surface of the cladding layer in Figure 1 (d).

3.2 Effect of Different Induction Currents on Cladding Layer

In this experiment, the output induction current intensity is proportional to the output power. The larger the induced current, the greater the output power and the more heat energy the sample receives. Four samples with graphene content of 0.3% were prepared by different induced currents. After induction cladding, the original structure of the coating surface was observed by scanning electron microscopy (SEM). The surface structure of the coating is shown in Figure 2.

![Figure 2 Surface morphology of cladding layers with different induced currents](image)

(a) 280A  (b) 320A  (c) 360A  (d) 400A

It is observed that when the induced current is 280A, a large number of unmelted particles can be seen on the surface of the cladding layer from Figure 2 (a). In Figure 2 (b), when the current rises to 320A, the unmelted stainless steel powder particles on the surface of the cladding layer decrease. It can be seen from Figure 2 (c) that there are no obvious unmelted powder particles on the surface of the cladding layer, and that the surface of the cladding layer is relatively flat, but there are still a few holes, which are caused by insufficient induction heating temperature; while Figure 2 (d) shows that there are a few over-burning phenomena on the surface, but the over-burning is not obvious. Induction cladding current is large and the temperature of induction heating is too high.

3.3 Metallographic analysis of cladding layer with different graphene content

Figure 3 is a photographed cross-section metallographic photomicrograph of the different graphene contents at an induced current of 360A. Compared to Figure3 (a) and (b), the cladding layers in Figure3 (c) and (d) are more dense and the grains are relatively small. The effect of graphene on the structure of cladding layer can be seen from Figure 3. In Figure 3, when graphene content is 0.2% and 0.3%, graphene migrates to the bonding zone and agglomerates during induction cladding. A small amount of oxides appeared in the cladding layer. In Figure 3 (c) Graphene content is 0.4%, the oxide content in the cladding layer increases, and the agglomeration of graphene is more obvious, which leads to the increase of defects in the cladding layer. However, graphene, originally near the bonding
zone, also appears in the cladding layer. The graphene content is 0.5% in Figure 3 (d). Because of the high content of graphene, the agglomeration of graphene near the bonding zone is intensified, and the oxide in the cladding layer is also more. At the same time, graphene diffuses to the matrix at high temperature, and the phenomenon of grain boundary oxidation appears in the matrix.

![Image of metallographic analysis](image)

Figure 3 Cross-sectional metallographic photos of samples with different graphene content (200X)
(a) 0.2% (b) 0.3% (c) 0.4% (d) 0.5%

### 3.4 Metallographic Analysis of Cladding Layer under Different Induction Heating Currents

Figure 4 is a metallographic photograph of different induced current intensities. The graphene content is 0.3%. The cross-sectional structure of the sample was divided into matrix and coating, and no obvious transition zone was observed. Graphene in the cladding layer migrates and agglomerates to the bonding zone.

In induction cladding, the surface temperature of the sample is very high. First, the coating melts by heat transfer. Because the melting point of Cr12MoV is lower than 316L stainless steel, the surface of the sample dissolves preferentially to form a molten pool, and there is oxidation more or less. The surface of the coating contacts with the external environment, which has the fastest heat dissipation, a large temperature gradient, and forms equiaxed crystals. The grain size becomes smaller and the structure is more compact.

Contrast diagrams Figure 4(a), (b), (c), (d) show that with the increase of induction current, the oxidation of the sample surface intensifies. The best cladding effect is that the induction current is 360A. At this time, there are fewer oxides in the cladding layer and fewer defects in the cladding layer.

![Image of metallographic analysis](image)

Figure 4. Metallographic micrographs of different induced current intensities (200X)
(a) 280A, (b) 320A, (c) 360A, (d) 400A
3.5 Effect of graphene content on mechanical properties

The purpose of this experiment is to study the effect of different graphene content on the hardness of metal coatings. The test parameters are set as follows: Four groups of samples are selected, and the induced current intensity is 360A. The graphene content was 0.2%, 0.3%, 0.4% and 0.5% respectively. Figure 5 shows Vickers hardness curve of graphene coatings with different content by induction cladding. The surface hardness of the cladding layer increased with the increase of graphene content. However, when graphene content reaches 0.5%, the slope of Vickers hardness curve decreases.

In the process of induction cladding, the hard phase with more graphene content precipitates, and the graphene in the coating distributes evenly. As the second phase, the hard phase also prevents the movement of dislocations and plays the role of pinning dislocations. Therefore, the hardness of the coating increases with the increase of graphene content. It is found that the increase of graphene content can significantly improve the microhardness of the coating. However, the agglomeration of graphene in the matrix leads to the increase of oxides in the cladding layer and the increase of defects in the cladding layer. The enhancement effect of graphene on the cladding layer is reduced. So when the graphene content is 0.5%, the slope of the curve in Vickers hardness decreases.

3.6 Effect of Different Induction Heating Currents on Mechanical Properties of Coatings

Figure 6 Hardness curves at different induced currents
The experimental scheme is as follows: using four groups of samples, the induced current intensity is 280 A, 320 A, 360 A and 400A respectively, and the content of graphene is 0.3%. Figure 6 shows the microhardness curves at different induction currents. Combined with metallographic images, when the current of induction cladding is 280-400A, the surface hardness of the cladding layer increases with the increase of current intensity. At the beginning, with the increase of induction current, the unmelted powder in the cladding layer decreases, and the bonding strength of the cladding layer surface increases. Therefore, the surface hardness of the cladding layer will be improved. However, when the induction current is 360A, graphene agglomeration occurs in the bonding zone of the cladding layer, and the defects in the cladding layer decrease, so the hardness of the cladding layer surface increases. When the induced current reaches 400A, a small amount of overburning occurs in the cladding layer, and obvious grain boundary oxidation occurs in the cladding layer. These oxides act as hard particles in the cladding layer, so the hardness of the cladding layer will continue to increase[6]. However, the existence of these oxides also leads to the decrease of the toughness of the cladding layer, which makes the material prone to fracture.

4 Conclusion
1. Graphene has obvious strengthening effect on the surface of cladding layer.
2. Graphene agglomerates at the bonding zone of the cladding layer. With the increase of graphene content, the defects such as oxides on the surface of the cladding layer also increase.
3. Different induction heating currents have great influence on the cladding effect. When the induction heating current is large, the surface of the cladding layer will appear obvious overburning phenomenon.

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