

Effect of CeO₂ on the Performance of Laser Cladding Coating of Ni-based Alloy

Y. Yang and L. Chen

Abstract—Laser cladding experiments are carried out using the mixed powders with different mass fraction of CeO₂. The physical properties of the cladding coating are analyzed, such as the surface morphology, crack sensitivity, dilution rate, wettability, and surface hardness. Further, the influence law of CeO₂ on the performance of laser cladding coating is studied. The results show that if the rare earth oxide CeO₂ is added into the Ni60A alloy powder, the crack sensitivity of cladding coating can be reduced, and the dilution rate of cladding coating can be decreased, also the hardness of cladding coating can be improved. However, the wettability of substrate is adversely affected. If the amount of CeO₂ is high, the surface quality of cladding coating will decrease, which cannot meet the requirements of application and processing. According to the experiments, it is concluded that the best addition amount of CeO₂ is 5%.

Index Terms—CeO₂, laser cladding, Ni based alloy, properties of coating.

I. INTRODUCTION

Laser cladding technology is becoming a new surface modification technology with the development of high power laser. The principle of it is that the alloy powder is placed on the surface of the cladding substrate in different filling ways, and uses laser as the heat source to rapidly melt alloy powder. Then forming a coating with excellent properties on the surface of the substrate, so as to achieve the purpose of strengthening the surface of the workpiece. Specially, the alloy powder of cladding coating directly determines the properties of the cladding coating.

Domestic and foreign scholars have done a lot of research on Laser Cladding Technology. For example, the Ni60 alloy was coated on surface of Q235 by Q. L. Yuan [1], and they through the means of the solid solution strengthening, dispersion strengthening, hard phase strengthening, and fine grain strengthening to enhance the surface properties of the parts. For another, the wear rate of dry friction of the Ni-Co based composite coating, prepared by X. M. Pan [2], decreased by 51% compared with the stainless steel substrate. What's more, the Ni and Co based materials were coated on the surface of Cr12MoV steel by D. Q. Dai [3], and the

results showed that the hardness and wear resistance of Ni-based coating were better than those of Co-based. Similarly, K. Q. Qi [4] prepared the Stellite6 cladding coating on the surface of H13 steel by CO₂ laser, and the results showed that the surface hardness of high temperature, wear resistance, corrosion resistance, and thermal fatigue resistance of the cladding coating were better than that of the substrate.

It has been found that the Ni-based alloy can be used to obtain the low crack cladding coating. However, now, the pure Ni-based alloy cladding coating cannot meet the requirements of the wear resistance, so it is need to be strengthened. In this paper, the CeO₂ strengthening phase is added to the Ni-based alloy powder of self fluxing to form the mixed powder, and then based on the properties analysis of the cladding coating formed by the mixed powder, the influence law of the CeO₂ strengthening phase on the properties of Ni-based alloy cladding coating is studied.

II. LASER CLADDING EXPERIMENTS

In the experiments, we use the LDF4000-60 semiconductor laser as the experimental instrument, the carburized 20CrMnTi steel as the substrate, and the Ni60A self fluxing alloy powder as the based powder.

The based powder composition are the C ($\leq 3\%$), Cr (12-19%), B ($\leq 2.3\%$), Si ($\leq 2.0\%$), Fe ($\leq 6\%$), and Ni (allowance). The particle size range of the based powder are 3.74×10^{-5} m to 7.50×10^{-5} m. The based powder shape are atomized sphere.

Six kinds of mixed powder are prepared by adding different amount of the rare earth oxide CeO₂ powder into the based powder. In the six mixed powders, the mass fraction of CeO₂ powder respectively is 0%, 1%, 3%, 5%, 8% and 15%, and the particle size of CeO₂ powder is less than or equal to 7.50×10^{-5} m.

Before the experiments, firstly, polishing the surface of the substrate with the 500# metallographic sandpaper to remove the surface oxide of the substrate. Secondly, wiping the surface of the substrate with absorbent cotton dipped in acetone to remove oil and polishing debris. Thirdly, drying the surface of the substrate with hot air blower. During the experiments, the laser cladding experiments are carried out after adjusting the process parameters of the LDF4000-60 semiconductor laser. The process parameters are the laser power (P) of 900 W, scanning speed (v) of 6 mm/s, and spot diameter (d) of 4 mm. After the experiments, the microhardness of the cladding coating is measured by the FM-700 microhardness tester, and the load is 300 g.

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III. EXPERIMENTAL RESULTS AND ANALYSIS

A. Surface Morphology of Cladding Coating

The macroscopic morphology images of Ni-based cladding coating with different mass fraction of rare earth oxide CeO_2 are shown in Table I. It can be seen from the images that the surface of the cladding coating appears many dark gray matters after adding the rare earth oxide CeO_2 . And with the increasing of the amount of CeO_2 in the Ni-based powder, the dark gray matters on the surface of the cladding coating are more and more. When the amount of CeO_2 reaches 15%, the surface of the cladding coating is almost covered by dark gray matters.

TABLE I: THE MACROSCOPIC MORPHOLOGY OF Ni60A+ CeO_2 CLADDING COATING

The Mass Fraction of CeO_2 in The Based Powder	The Morphology of The Cladding Coating before Sanding	The Morphology of The Cladding Coating after Sanding
0%		
1%		
3%		
5%		
8%		
15%		

In order to find out the cause of the formation of the dark gray matters, the laser cladding coating of pure CeO_2 powder is prepared, and the macroscopic morphology of CeO_2 cladding coating is shown in Fig. 1.



Fig. 1. Surface morphology of CeO_2 powder cladding coating.

Compared the images in Table I and Fig. 1, the color of the pure CeO_2 cladding coating is consistent with the color of the dark gray matters on the Ni-based cladding coating with CeO_2 addition. Therefore, it is believed that the dark gray matters, appeared on the surface of the Ni-based cladding coating with CeO_2 addition, is the CeO_2 powder which is gathered together. Next considering that the proportion of CeO_2 powder in the mixed powder is small, it is possible to distribute unevenly, so prolonging the milling time of the mixed power. However, the experimental results show that

prolonging the milling time cannot solve this problem effectively.

In the process of treating, the dark gray matters mostly from the cladding coating off when sanding the cladding coating. After the treatment, the cladding coating is continuously unbroken, and the main surface of the cladding coating still shows bright metallic color. But the surface of the cladding coating leaves obvious defects due to the falling of the CeO_2 matter which is gathered together, and it affects the surface quality of cladding coating.

Therefore, according to the surface quality of the cladding coating, the optimum adding amount of CeO_2 is 1% or 5%.

B. Crack Sensitivity of Cladding Coating

In the cladding coating, it appears a kind of crack which is transversal penetrating the coating. This situation mainly occurs in the solidification process of the cladding coating, and accompanies a clear sound of rupture. According to the research result of M. L. Zhong [5], it shows that this kind of crack of cladding coating belongs to the cold crack and it is mainly caused by thermal stress. When the strain (ε) exceeds the local regional plasticity (δ_{min}) of the materials, the materials of cladding coating will be fractured. The formula for calculating crack rate is as follows:

$$k = \frac{n}{l} \times 100\% \quad (1)$$

Annotation: k --- the crack rate, n --- the number of transverse crack, l --- the length of cladding coating.

The crack rate is calculated by using (1), and the relationship between the crack rate of cladding coating and the CeO_2 addition of the different mass fraction is shown in Fig. 2.

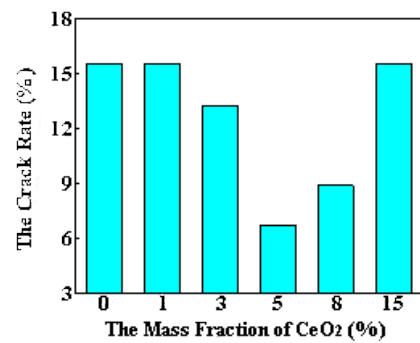


Fig. 2. The relationship between the crack rate of cladding coating and the CeO_2 addition of the different mass fraction.

According to the change trend of the crack rate in Fig. 2, it is found that with the increase of the mass fraction of CeO_2 , the crack rate of the cladding coating is the first to fall. When the mass fraction of CeO_2 is 5%, the crack rate of the cladding coating is 6.7%, which reaches the lowest level of the crack rate of the cladding coating, and decreases by about 8.9% compared with that without adding CeO_2 . If the addition of CeO_2 continues to increase, the crack rate will rise, but the crack rate of the cladding coating is still lower than that without adding CeO_2 . When the mass fraction of CeO_2 is up to 15%, the CeO_2 will have no effect on the crack rate of the cladding coating.

Ce, which is similar to other rare earth elements, has a very active chemical properties. In the process of laser heating, the Ce element will be combined with harmful elements, such as the S, O, and H, to form a stable rare earth compound in the cladding coating. It can reduce the combination of harmful elements and other elements of the cladding coating, improve the uniformity of the microstructure in the cladding coating, and relieve the residual stress and concentrated stress, so that the crack initiation probability can be decreased.

At the same time, the rare earth element also has the effect of refining the microstructure grain. To some extent when the grain is refined, the resistance between the grain boundaries is increased and the crack propagation is restrained, which can reduce the cracking tendency of the cladding coating. In addition, some studies have shown that the addition of CeO₂ in Ni-based cladding materials will increase the proportion of the equiaxed grain in cladding coating. If the microstructure morphology is dendrite, the bonding strength of the contact surface is relatively weak. The non-metallic impurities and the low melting point impurities are also easily gathered here, which may be the cause of crack formation and expansion in the solidification process of cladding coating. On the contrary, the equiaxed grain plays an important role in inhibiting the crack formation and expansion. Because the grain size of equiaxed grain is similar in each direction and the bonding strength of equiaxed grain is higher, it will not appear the situation of preferred orientation.

Therefore, according to the crack sensitivity of cladding coating, the optimum adding amount of CeO₂ is 5%.

C. Dilution Rate of Cladding Coating

Dilution rate is also an important factor to reflect the quality of cladding coating. The simplified formula for calculating dilution rate is as follows [6]:

$$\eta = \frac{h}{H + h} \times 100\% \quad (2)$$

Annotation: η --- the dilution rate, h --- the melting depth of substrate, H --- the height of cladding coating.

Using the stereo microscope to measure the height of cladding coating and the melting depth of substrate. Then the dilution rate is calculated by using (2), and the relationship between the dilution rate of cladding coating and the CeO₂ addition of the different mass fraction is shown in Fig. 3.

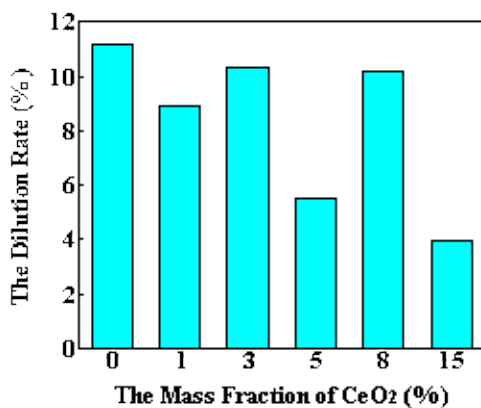


Fig. 3. The relationship between the dilution rate of cladding coating and the CeO₂ addition of the different mass fraction.

According to the overall situation in Fig. 3, the addition of CeO₂ can effectively reduce the dilution rate of Ni-based cladding coating under the same laser process parameters. When the addition amount of CeO₂ is 15%, the dilution rate of the cladding coating is 3.98% which is very small.

The dilution rate is small, which means the depth of molten pool can be decreased, so that the quality of cladding coating can be better. After adding the rare earth oxide CeO₂ into the cladding material, the latent heat of fusion of the cladding material can be increased. The reason is that it makes the solidus of the cladding material rise and the liquidus of the cladding material decrease, so that the size of the molten pool is reduced. At the same time, the solidification time of the molten pool is shorter, and the large-scale diffusion between the substrate and the cladding coating cannot be carried out. Finally, the dilution rate of cladding coating is reduced.

Therefore, according to the dilution rate of cladding coating, the optimum adding amount of CeO₂ is 15% or 5%.

D. Wettability of Substrate

According to the geometry of cladding coating, the wettability of substrate can be obtained by measuring the contact angle between the cladding coating and the substrate. The formula for calculating the contact angle is as follows.

$$\sin \theta = \frac{H}{W} \left[\left(\frac{H}{W} \right)^2 + 0.25 \right] \quad (3)$$

Annotation: θ --- the contact angle between the cladding coating and the substrate, H --- the height of cladding coating, W --- the width of cladding coating.

The contact angle is calculated by using (3), and the numerical solutions of contact angle when adding different mass fraction of CeO₂ are shown in Table II.

TABLE II: THE CONTACT ANGLE OF Ni60A+ CeO₂ CLADDING COATING

The Mass Fraction of CeO ₂ in The Based Powder	The Contact Angle (θ)
0%	121.52°
1%	110.21°
3%	115.50°
5%	112.85°
8%	114.63°
15%	112.54°

The data of Table II shows that the contact angles are decreased after adding the CeO₂ in the Ni-based powders. For example, when the addition amount of CeO₂ is 3%, the contact angle is 115.50°, which is reduced by 6.02° compared with that without adding CeO₂. Similarly, when the addition amount of CeO₂ is 1%, the contact angle is 110.21°, which is reduced by 11.31° compared with that without adding CeO₂.

After adding the CeO₂, the ratio of height and width of cladding coating is increased, which makes the cladding coating shape become high and thin. So, there may be a running hole during the multipass cladding, which will affect the quality of cladding coating, but the contact angle can be improved by increasing the laser power or decreasing the scanning speed to reduce this bad effect.

Therefore, under this experimental conditions, the addition of CeO_2 will have an adverse effect on the wettability of substrate.

E. Surface Hardness of Cladding Coating

The average hardness of the cladding coating is calculated by the means of six points method, and the relationship between the surface hardness of cladding coating and the CeO_2 addition of the different mass fraction is shown in Fig. 4.

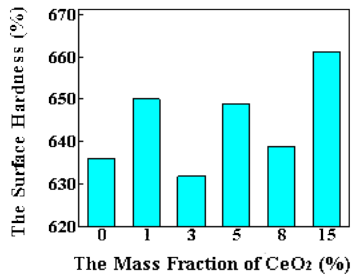


Fig. 4. The relationship between the surface hardness of cladding coating and the CeO_2 addition of the different mass fraction.

As can be seen from Fig. 4, after the addition of CeO_2 , the surface hardness of the cladding coating is increased except for the addition amount of CeO_2 is 3%, and it can be improved by 3-25 $\text{HV}_{0.2}$.

Ce, which is in the CeO_2 , can limit the growth of grain to refine and strengthen the cladding coating. The principle is that with the decrease of grain size, the ratio of surface area and volume of the grain becomes larger, so that the surface tension is increased and the crystal lattice near it is deformed. Then it forms a hard deformation zone where the grain is not easy to deform. And the smaller the grain size is, the larger the hard deformation zone will be, which results in the increase of the deformation resistance. Thus, the surface hardness of cladding coating is improved. In addition, the diffusion of rare earth elements also affects the crystal lattice size, which can achieve the solution strength and form a certain number of hard phases. And these chemical compounds will be distributed at the grain boundaries to purify and strengthen it. On the other hand, Ce can make the structure more uniform and reduce the difference of the hardness values of each part in the cladding coating.

Therefore, according to the surface hardness of cladding coating, the optimum adding amount of CeO_2 is 1%, 5%, or 15%.

Based on the above experimental results and analysis, the conclusions can be draw that the best addition amount of CeO_2 is 5% in the experiments. In this situation, the surface morphology of cladding coating is good, the crack sensitivity of cladding coating is the lowest, the dilution rate of the cladding coating is decreased, the adverse effect on the wettability of substrate is the least, and the surface hardness is increased to 649 $\text{HV}_{0.2}$.

IV. CONCLUSION

In this paper, the effect of CeO_2 on the performance of

laser cladding coating of Ni-based alloy is studied by a lot of experiments.

The laser cladding experiments are carried out by adding the different mass fraction of CeO_2 into the based powder. Further, the surface morphology, crack sensitivity, dilution rate, wettability of substrate, and surface hardness are researched and analyzed.

The results show that if adding rare earth oxide CeO_2 into Ni60A alloy powder, the crack sensitivity of cladding coating can be reduced. According to the experiment results, the best addition amount of CeO_2 is 5%.

It also points out that adding CeO_2 strengthening phase into Ni-based alloy powder can improve the performance of laser cladding coating of Ni-based alloy, which lays a foundation for the high efficiency laser cladding technology of the 20CrMnTi steel.

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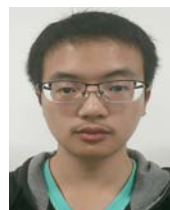
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