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Research Status of Addition and Application of Different Rare Earth Elements in Laser Cladding and Their Effects on Properties and Structures

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ABSTRACT

Laser cladding technology, as an efficient material surface modification technique, has seen widespread application in the industrial field in recent years. Rare earth elements, with their unique physical and chemical properties, have demonstrated significant advantages in laser cladding materials. Firstly, rare earth elements can significantly enhance the hardness, wear resistance, and corrosion resistance of the clad layer, thereby extending the service life of components. Secondly, rare earth elements can improve the micro-structure and bonding strength of the clad layer, enhancing overall mechanical performance. Additionally, rare earth elements can act as deodorizers during the laser cladding process, increasing the purity and quality of the cladding material. However, the addition of rare earth elements also brings some technical challenges, such as uneven element distribution and high costs. Currently, optimizing the application of rare earth elements in laser cladding to achieve a balance between material performance and cost remains a key research direction. Through further exploration and innovation, the potential of rare earth elements in laser cladding will be more broadly realized.

KEYWORDS

Laser cladding; Rare earth elements; Micro-structure; Bond strength

1. INTRODUCTION

As industrial development progresses, more and more materials struggle to meet the demands of harsh environments. To address these issues, various surface technologies have been employed to enhance material surface properties [1]. Current surface technologies include thermal spraying, physical vapor deposition, electroplating, ion implantation, and plasma cladding. Thermal spraying suffers from significant material wastage and low adhesion; electroplated coatings are thin with low bonding strength to the substrate; plasma cladding significantly affects substrate deformation; ion implantation requires specific part shapes and has high equipment costs. In contrast, laser cladding offers advantages such as a small heat-affected zone, minimal deformation, rapid cooling rate, dense microstructure, low dilution rate, metallurgical bonding with the substrate, and a wide range of material applications. Therefore, it has a promising application prospect [2].

Currently, laser cladding self-fluxing alloy powders mainly include cobalt-based, nickel-based, and iron-based systems. To enhance the hardness and wear resistance of coatings, ceramic phases are commonly added. However, the significant difference in thermal expansion coefficients between the ceramic phases and the substrate can cause the coatings to peel off. When the ceramic phase content is high, the hardness of the coating increases, but the brittleness also rises, leading to crack formation under applied tensile stress. Research indicates that as the ceramic phase content increases, the corrosion resistance of the coating decreases [3]. Additionally, micro-defects such as pores formed during laser cladding can serve as stress concentrators, which may propagate into cracks under tensile stress [4]. Methods like preheating, heat treatment, or applying auxiliary fields during cladding can effectively improve cladding defects, but they increase processing time and cost. Extensive research shows that adding a suitable amount of rare earth elements to the cladding layer can significantly prevent defects, refine and purify the microstructure, strengthen grain boundaries, and potentially reduce the dilution rate, thereby markedly enhancing the surface hardness, wear resistance, and corrosion resistance of the cladding layer [5].

Rare earth elements, known as the "vitamins of metals" due to their exceptional properties, are widely used in aerospace, chemical engineering, metallurgy, and other fields. Currently, researchers both domestically and internationally have conducted studies on the application of rare earth elements in laser cladding, leading to significant improvements in the performance of laser-clad coatings. This paper analyzes the mechanisms by which rare earth elements function in laser cladding, summarizes the current application status and performance comparisons of rare earth elements in laser cladding, and aims to provide a reference for related research work.

2. STRENGTHENING MECHANISM OF RARE EARTH IN LASER CLADDING

2.1. The Effect of Molten Pool

Rare earth oxides play a role in enhancing the convection within the molten pool. Variations in the content of rare earth elements can influence the rate at which the cladding layer absorbs laser energy. Appropriate amounts of rare earth oxides can improve the fluidity of the molten pool, leading to a more uniform distribution of coating elements, and can reduce nucleation work, thereby increasing the number of nuclei [6]. Excessive rare earth oxides, however, react with impurity elements to form a large quantity of refractory rare earth compounds, thereby reducing the fluidity of the molten pool and causing uneven element distribution within the coating layer. This can result in segregation of the coating's chemical composition, as well as an increased likelihood of incomplete removal of impurities and gases, contributing to the presence of voids and cracks. Additionally, it can slow down the cooling rate of the molten pool, promoting grain growth.

2.2. Effect of Dilution Rate

To achieve good cladding quality in laser cladding, it is typically necessary to have a minimum dilution rate and strong metallurgical bonding between the coating and the substrate. Studies have shown that rare earth elements can potentially reduce the dilution rate. The addition of rare earth elements increases the latent heat of melting of the alloy, thereby lowering the liquidus temperature and increasing the solidus temperature. Consequently, the solidification time and solidification range of the coating are shortened, ultimately inhibiting the diffusion of elements between the coating and the substrate [7].

2.3. Thermal Decomposition

Due to the high-energy, high-temperature effects of laser heating, some of the rare earth oxides in the coating decompose into rare earth atoms (such as Ce, La, and Y) and oxygen atoms. The decomposed rare earth atoms, which exhibit strong surface activity, can reduce surface tension and have low electronegativity. These atoms can react with O, H, S, and other impurity elements in the molten metal to form high melting point, low-density, and relatively stable rare earth compounds (such as Ce_2O_2S, CeFeSi, $LaCrO_4$, and Ce_2Co_{17}), thereby suppressing structural looseness. Some of these rare earth compounds and un-melted rare earth oxides can serve as heterogeneous nucleation sites, increasing the nucleation rate and the number of nuclei, or they can segregate at grain boundaries, strengthening the boundaries and inhibiting grain growth, thus refining the grains. Additionally, a portion of these compounds' forms slag under the laser action, which floats on the liquid phase before solidification, carrying away gases and impurities from the molten pool, thereby purifying the coating.

2.4. Characteristics of Rare Earth Elements

Due to the relatively large atomic radii of rare earth elements, typically ranging from 0.713 to 0.204 nm [8], and their strong surface activity, they primarily distribute along the grain boundaries. As the grains grow, rare earth atoms and compounds exert a dragging effect on the grain boundary movement. This difficulty in grain boundary movement inhibits grain growth, leading to grain refinement [9]. Simultaneously, during solidification, rare earth atoms tend to concentrate in the liquid phase at the liquid-solid interface, increasing undercooling and accelerating dendrite formation, which reduces grain size and enhances strength and toughness. The high reactivity of rare earth elements also improves the alloy's oxidation resistance [10].

3. APPLICATION OF RARE EARTH IN LASER CLADDING

At present, the rare earth additives introduced into laser cladding materials mainly include three types: pure rare earth elements, rare earth oxides, and rare earth compounds. The addition of rare earths can refine grains, reduce the formation of pores and cracks, thus improving hardness and wear resistance. From the wear morphology perspective, the incorporation of rare earths can prevent severe plastic deformation, adhesive wear, fatigue wear, and abrasive wear, resulting in only minor scratches, and the wear traces appear less severe. The improvement in the fracture toughness of the coating is attributed to an increase in the total grain boundary area, a reduction in lattice distortion, a decrease in impurity concentration at the grain boundaries, and a lower dislocation density [7]. Adding rare earths can enhance the distribution of corrosion-resistant elements like Ni and Cr within the coating, and can also help form a dense and uniform passivation film, thereby improving corrosion resistance. Existing research shows that, regardless of the form in which rare earths are added, they generally have a positive impact on the microstructure and properties of the coatings.

3.1. Application of Pure Rare Earth Elements

Rare earth elements are surface-active elements that tend to react easily with harmful elements such as oxygen, nitrogen, and sulfur in the molten pool, forming high melting point, low-density compounds. These compounds float to the surface of the liquid phase before solidification and appear as slag on the surface of the cladding layer. Weng et al. [11] found that adding 0.4 wt% La to a WC/Ni-based composite coating resulted in a coating without cracks and porosity, but had almost no effect on hardness. Zhang Jian et al. used laser cladding technology to prepare high-boron iron-based alloy coatings with different Ce contents on a 45 steel substrate. After adding Ce, the grain size of the coating decreased, and with the increase in Ce content, the fracture toughness of the coating first increased and then decreased, while the friction coefficient first decreased and then increased.

Due to the highly reactive nature of Y, it cannot stably exist in the coating during the laser cladding process and tends to react with oxygen, forming stable Y_2O_3. Additionally, the inclusion of Y can increase the volume fraction of the eutectic phase, thereby enhancing the bulk phase. Li et al. [12] studied the effects of Y on the microstructure and mechanical properties of in-situ synthesized TiB and TiC laser cladding layers. They found that adding Y reduced the size of the cellular dendrites, accelerated their spheroidization and refinement, increased hardness, and reduced the sensitivity to cracking.

Adding an appropriate amount of pure rare earth elements to laser cladding materials can produce coatings with good forming quality and fine grains, while also improving mechanical and tribological properties.

3.2. Application of Rare Earth Oxides

Currently, the rare earth oxides used in laser cladding primarily include CeO_2, La_2O_3, and Y_2O_3. The optimal addition amount of rare earth oxides is a key area of research. Numerous studies have shown that each rare earth oxide has an optimal addition amount; excessive addition not only results in the waste of rare earth resources but can also negatively impact the performance of the coating. While the addition of rare earth oxides has little effect on the phase composition of the coating, the appropriate amount of rare earth oxides can significantly improve the wear resistance, corrosion resistance, and toughness of the coating by enhancing its microstructure and reducing dilution rates.

3.2.1. CeO_2 addition

Guangyao Zhang et al. prepared a Ni60 alloy coating with 5wt% CeO_2 added on the surface of a 6063 aluminum substrate. Compared to the coating without CeO_2, the addition of CeO_2 effectively reduced cracks and pores in the coating, lowered the dilution rate, and significantly refined the microstructure. Research has shown that CeO_2 not only enhances hardness but also makes the distribution of hardness more uniform. Peng Xue et al. prepared a TC_4+Ni45 composite coating on the surface of Ti811 alloy. Compared to the coating without CeO_2, adding 3wt% CeO_2 did not change the main phases of the coating, but the microstructure was significantly refined, and the hardness distribution was more uniform and significantly improved.

However, the above studies did not systematically investigate the impact of different addition amounts on the coating's microstructure and performance. Comparative studies should be conducted to evaluate the effect of varying the addition amount on the coating properties to determine the optimal addition amount. Studies have shown that CeO_2 has an optimal addition amount, and exceeding this optimal value will degrade the coating's performance. Ding et al. prepared Co-based composite coatings with different nano CeO_2 contents on the surface of SPHC steel. The coatings exhibited excellent surface quality, and with the increase of nano CeO_2 content, the hardness and wear resistance of the coatings first increased and then decreased, reaching the best performance at 1.5wt% CeO_2.

Huahuan Xu et al. investigated the effect of adding 0-2.0wt% CeO_2 on the phase composition and performance of WC/Ni-based alloy coatings on the surface of 42CrMo steel substrates. After adding CeO_2, a small amount of $CeNi_3$ appeared in the coating, and the best hardness and wear resistance were achieved at 1.0wt% CeO_2. Wang et al. laser cladded WC-reinforced aluminum-based coatings containing CeO_2 on the surface of S420 steel. The results showed that when the CeO_2 content was 1wt%, the grain refinement effect was significant, the impact toughness improved, and the corrosion resistance was the best.

Adding CeO_2 in appropriate amounts can refine the crystal structure, improve the chemical composition heterogeneity, purify the crystal structure, and delay the grain boundary corrosion rate. CeO_2 can increase the content and distribution of corrosion-resistant elements such as Ni and Ti in the coating, making the passivation film denser and more uniform, thereby improving the coating's corrosion resistance. CeO_2 also plays an important role in the tensile properties of coatings. Sun et al. prepared (Ti, Nb)C/Ni-based coatings with different CeO_2 contents. The results showed that Ce inhibited the grain size of (Ti, Nb)C reinforcing particles, and the unmelted CeO_2 acted as a heterogeneous nucleation site for (Ti, Nb)C, $Cr_{23}C_6$, and Cr_7C_3. Additionally, CeO_2 affected the growth orientation of grains in the coating, and the tensile properties of the coating improved with increasing CeO_2 content.

In summary, the appropriate addition of CeO_2 can significantly improve various properties of the coating, but the optimal addition amount must be found for each specific application to avoid resource waste and performance degradation due to over-addition.

3.2.2. La_2O_3 addition

In addition to positively impacting the microstructure and properties of coatings, adding La2O3 can also reduce machining vibrations by enhancing the damping capacity of the coating. Zhao et al. used Fe-Cr alloy mixed with La_2O_3 powders to create a laser cladding layer on KMN steel plates and studied the effects of different La_2O_3 mass fractions on the coating's performance. They found that with increasing La_2O_3 content, the hardness and wear resistance of the coating increased, while machining vibrations initially decreased significantly and then increased with further La_2O_3 additions.

An appropriate amount of La_2O_3 improves coating hardness and wear resistance by mitigating cracks and refining grains. Min Li added different amounts of La_2O_3 to cobalt-based alloy powders and created cladding coatings on Q235 substrates. The results indicated that there is an optimal range for the rare earth addition amount, which is 3wt% for La_2O_3. At this concentration, the microstructure was finest and densest, and the performance was optimal. Wang et al. used laser cladding technology to prepare iron-based composite coatings with added La_2O_3 on a 45 steel substrate, studying the effects of different La_2O_3 contents on the coating's microstructure and properties. When the La_2O_3 content was 1wt%, grain refinement and dispersion strengthening by La_2O3 significantly improved the hardness and wear resistance of the coating. La_2O_3 also increased the fluidity of the molten metal in the melt pool, resulting in a more uniform distribution of elements within the coating.

Liang Zhang et al. prepared 304L coatings with different La_2O3 contents on a 45 steel substrate. They found that adding La_2O_3 caused the carbon from the 45 steel to melt into the clad layer and combine with the iron from the 304L powder to form more $CFe_{2.5}$, with the $CFe_{2.5}$ peak increasing. The microstructure was most uniform, and performance was optimal when the La_2O_3 addition was 1.0wt%.La_2O_3 also has a positive impact on the corrosion resistance of coatings. Li et al. used laser cladding technology to create La_2O_3-containing nickel-based alloy coatings on medium carbon steel surfaces. When the La_2O_3 addition was 0.6wt%, the resulting nickel-based composite coating was crack-free, and the corrosion current density was reduced, enhancing the corrosion resistance.

In summary, adding La_2O_3 can reduce machining vibrations, making it significant for repairing mechanical parts, such as gear teeth surfaces, using laser cladding technology. An appropriate amount of La_2O_3 can improve various coating properties by mitigating defects, refining grain structure, and ensuring uniform elemental distribution.

3.2.3. Y_2O_3 addition

Iron-based alloy coatings are cost-effective but have poor high-temperature oxidation resistance, limiting their industrial applications. Adding Y_2O_3 can improve the high-temperature oxidation resistance of iron-based alloys. Zhang et al. [18] prepared Y_2O_3-containing ceramic-reinforced iron-based composite coatings on the surface of 5CrNiMo steel using laser cladding technology. They found that Y_2O_3 can refine the ceramic particles and microstructure of the coating, and at an addition of 2wt%, it enhanced the continuity and density of the surface oxide layer, thereby improving the high-temperature oxidation resistance of the coating. An appropriate amount of Y_2O_3 can also increase the coating's hardness and wear resistance.

Weng et al. [19] used laser cladding technology to prepare Y_2O_3-containing TiN-reinforced Co-based composite coatings on a Ti6Al4V titanium alloy substrate. They found that adding 1.0wt% Y_2O_3 additive could refine the coating grains, enhance wear resistance and hardness, and result in a coating free from cracks and pores. The presence of un-melted Y_2O_3 and free Y atoms formed by the decomposition of Y_2O_3 were the main reasons for the improved performance of the coating.

Liu Jia and colleagues prepared Y_2O_3-containing Ni-based WC composite coatings on the surface of 40Cr10Si2Mo steel. The addition of rare earth oxides improved the melt pool fluidity without changing the phase composition. The coating with 1.0wt% Y_2O_3 had the finest microstructure and the best hardness and wear resistance.

Yang et al. [20] added Y_2O_3 powder and WC powder as reinforcing phases to H_{13} powder and cladded it on the surface of 8407 steel. The addition of Y_2O_3 improved the uniformity of hardness distribution in the coating. The hardness trend during high-temperature holding was similar to that of 8407 steel but exhibited better performance. These studies collectively show that appropriate amounts of Y_2O_3 increase the absorption of laser energy by melt pool materials, mainly by reducing element diffusion from the substrate, promoting grain refinement, and improving melt pool convection to uniformly distribute the reinforcing phase, thereby enhancing coating hardness. Increasing the coating thickness can improve its service life, and adding Y_2O_3 can increase the coating thickness.

Zhang et al. [21] studied the effect of Y_2O3 addition on laser-cladded titanium alloy coating quality, microstructure, and microhardness. They found that without Y_2O_3, the coating thickness was about 600-740 μm with significant porosity. With 2wt% Y_2O_3, the thickness increased to 710-820 μm without visible pores. Due to grain boundary strengthening, grain refinement, and pore elimination, hardness and wear resistance increased.

Y_2O_3 can reduce the temperature gradient. Du et al. [22] studied composite coatings with different Y_2O_3 additions (0, 1, 3, and 5 wt%) on the surface of Invar alloy. They noted that with Y_2O_3 addition, the microhardness of the coating decreased, and the hardness gradient decreased with increasing Y_2O_3 content. The glow in the melt pool became more pronounced with higher Y_2O_3 content. The decreased hardness might be due to not finding the optimal rare earth addition amount. Some studies suggest that the optimal rare earth content is between 0.3wt% and 1.0wt%, indicating the need for further research on the effect of this range on microhardness.

In summary, adding Y_2O_3 positively impacts hardness and wear resistance and increases coating thickness while promoting carbide decomposition and uniform distribution, reducing hardness gradient. At high temperatures, Y_2O_3 also positively affects coating performance. The phenomenon of a brighter glow in the melt pool with increasing Y_2O_3 content needs further investigation to understand the underlying causes.

4. EFFECTS OF DIFFERENT TYPES OF RARE EARTH ON LASER CLADDING PROPERTIES

4.1. Comparison of Properties of Different Rare Earth Oxides

Wang et al. [39] utilized laser cladding technology to prepare Ni60 alloy coatings with the addition of La_2O_3, Y_2O_3, and CeO_2 on the surface of 6063Al substrates. After the addition of rare earth oxides, chemical reactions occur during the cladding process, forming stable rare earth compounds. This results in a dense and uniform microstructure, significant grain refinement, and improved hardness and wear resistance. The coating with CeO_2 has the lowest friction coefficient, and the coatings with La_2O_3 and CeO_2 exhibit the best wear resistance. Wang Chenglei et al. prepared Ni60 alloy coatings reinforced with 4wt% CeO_2, 5wt% Y_2O_3, and La_2O_3 on the surface of 6063 aluminum alloy substrates and studied the hardness and high-temperature (100°C, 300°C, 500°C) friction and wear performance of the coatings. The results showed that the Ni60 alloy coating with 4wt% CeO_2 had the best hardness and wear resistance. Xu et al. [24] studied the effects of 2wt% CeO_2 and La_2O_3 on the microstructure and corrosion behavior of laser clad 316L stainless steel coatings. The addition of rare earth oxides led to grain refinement and improved corrosion resistance of the coating. The CeO_2 modified laser-clad layer performed better than the La_2O_3 modified layer.

In summary, according to current research, it is generally believed that compared to Y_2O_3 and La_2O_3, CeO_2 has a better effect on improving or suppressing microcracks and enhancing performance.

4.2. Comparison of Pure Y and Y2O3

Li et al. investigated the effects of pure Y and Y_2O_3 on the microstructure and properties of Ni45 coatings to improve their performance. The results showed that pure Y reacts with O_2 to release a large amount of heat energy, while the heat generated by Y_2O_3 in the molten pool is relatively low. Therefore, the pure Y molten pool has a higher flow rate. Pure Y can inhibit grain growth, but the extended presence of the molten pool significantly refines the coating, leading to the precipitation of hard phases and increased brittleness, thereby enhancing wear resistance but limiting impact resistance and corrosion resistance. On the other hand, Y_2O_3 not only hinders grain growth but also acts as heterogeneous nucleation sites, increasing the nucleation rate, refining the microstructure, and suppressing the precipitation of hard phases. The wear resistance of Y_2O_3-coated layers is lower than that of pure Y-coated layers, but the impact and corrosion resistance are superior to those of pure Y-coated layers. The application of pure Y and Y_2O_3 in laser cladding primarily affects the molten pool flow rate and microstructure, thereby producing different effects on the coating's properties.

4.3. Comparison of Powder Size

The particle size of rare earth powders also has a significant impact on the microstructure and properties of laser-clad coatings. The hardness and wear resistance of the coatings increase with the reduction in CeO_2 powder particle size. Compared to micron-sized rare earth oxides, nano-sized rare earth oxides have finer and denser microstructures, resulting in better performance. Zhang et al. [25] used laser cladding technology to add micron and nano CeO_2 powders to a nickel-based alloy. The 1.5wt% nano CeO_2/Ni-based coating exhibited the best hardness and wear resistance. In the micron CeO_2/Ni-based coating, directional dendrites and coarse equiaxed dendrites grew from the interface to the central area, whereas the addition of nano CeO_2 resulted in the growth of multidirectional dendrites and fine equiaxed dendrites. The particle size of rare earth powders can affect the coating's microstructure, hardness, and wear resistance. However, current research on rare earth powder particle size is relatively scarce, and studies on the effects of particle size on properties such as corrosion resistance, impact resistance, and bonding strength are lacking.

5. CONCLUSION

Existing studies generally indicate that the addition of rare earth elements can improve cladding defects, refine grains, purify the microstructure, and potentially reduce dilution rates, thereby enhancing the hardness, wear resistance, and corrosion resistance of the clad layer, while also increasing its strength and toughness. However, there is still a lack of research on the effects of rare earth elements on the bonding strength between the coating and the substrate, as well as the underlying mechanisms.

There is an optimal range for the addition of rare earth elements; an appropriate amount can effectively enhance the performance of the clad layer, whereas excessive rare earth can reduce the performance of the laser cladding layer. Additionally, compared to micron-scale rare earths, nano-scale rare earths can achieve finer and denser microstructures, resulting in better hardness and wear resistance of the coatings. CeO_2 is more effective than Y_2O_3 and La_2O_3 in improving or suppressing microcracks in the laser cladding layer and enhancing performance; coatings prepared with pure Y exhibit good wear resistance, while Y_2O_3 coatings have superior impact and corrosion resistance.

Current research mainly focuses on rare earth elements such as lanthanum, cerium, and yttrium. Many other rare earth elements have yet to be applied in laser cladding. Future research can expand the selection of rare earth elements and further explore their applications in laser cladding.

CONFLICTS OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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