Optics and Lasers in Engineering 93 (2017) 195–210

Contents lists available at ScienceDirect

Optics and Lasers in Engineering

journal homepage: www.elsevier.com/locate/optlaseng

Research and development status of laser cladding on magnesium alloys: A review

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ARTICLE INFO

Keywords:
Magnesium alloys
Laser cladding
Material systems
Development tendency

ABSTRACT

Magnesium alloys are one of the most promising lightweight structural materials. However, the poor corrosion and wear resistance restrain their further application. As a kind of surface modification technique, laser cladding treatment is superior to others owing to its unique characteristics such as high efficiency and the metallurgical bonding between the coatings and substrates. In this paper, the laser cladding process and the effects of processing parameters, including laser power, scanning velocity, beam focal position, feeding ways of the material etc., are discussed in detail. The material systems preplaced on magnesium alloys are summarized. Except for the traditional metallic materials, novel ternary alloys, amorphous alloys and high entropy alloys (HEAs) are widely used and apparent advantages are exhibited. In terms of the problems existing in the laser cladding process of magnesium alloys, some potential solutions and the development tendency are reviewed.

1. Introduction

Magnesium alloys have developed into one of the most promising candidates as structural materials [1–3]. They have good castability, machinability, high strength-to-weight ratio, and some advantages in price due to the abundant reserves on the earth and in the sea [4]. Magnesium alloys, whose densities are approximately 35% smaller than that of aluminum alloys and 65% smaller than that of titanium alloys [5], have been widely used in the fields of automotive and aerospace. Magnesium alloys are increasingly used in fabricating certain parts in automotive field, such as engine block, steering wheel frame, seat frame, and so on [6]. Exceptionally, the excellent electromagnetic shielding and damping capacities make them better properties of protecting signal and reducing the noise, and gradually replace the plastic in electronic industries [7]. However, poor galvanic corrosion characteristic [8] shortens the service lives of magnesium alloys parts under certain application circumstances, especially in wet and salt-laden environments. Similarly, the poor wear resistance [9] and high-temperature stability [10] inhibit their further applications in industries.

Nowadays, relevant researches are needed on magnesium processing, alloying and surface treatment techniques [6]. Various surface modification techniques have been adopted to enhance the mechanical properties of magnesium alloys, such as chemical conversion [11], physical vapor deposition (PVD) [12,13], chemical vapor deposition (CVD) [14], micro-arc oxidation (MAO) [15,16] or plasma electrolytic oxidation (PEO) [17], diffusion treatment [18], electroless plating [19], and so on. Jiang et al. [11] fabricated Ce-V conversion coating on AZ31 magnesium alloy. The coating contained amorphous microstructure, and showed better corrosion resistance than the as-received substrate. However, cracks formed on the surface and a double-layer structure was observed owing to the different elementary composition, which was detrimental to the properties of the coating. Mao et al. [12] reported certain behaviors of the carbon film with electroless nickel interlayer (Ni+C) on GW83 (Mg-8Gd-3Y-0.5Zr) magnesium alloy deposited by PVD. Though the method solved the common problem like low adhesion force between the coating and substrate in some extent, the thin and porous carbon film was prone to form galvanic cells and it was disadvantageous to enhance the property of corrosion resistance.

In recent decades, laser has been widely used in material cutting and manufacturing processes owing to its high energy density [20–23], and the laser surface treatment has been a research hotspot. Laser surface treatments, including laser alloying [24], laser remelting [25], laser cladding [26], laser shot peening [27], and so on, have gone through rapid developments owing to their many particular advantages. The

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http://dx.doi.org/10.1016/j.optlaseng.2017.02.007
Received 19 November 2016; Accepted 13 February 2017

treatments would develop coatings on the surface without damaging the shape and inherent properties of the bulk materials, but having the effects of surface modification or strengthening, sometimes realizing surface repairing [28]. Especially, laser cladding has some brilliant advantages. Firstly, the coatings show strong metallurgical bonding with substrate with a shallow heat affected zone. Secondly, the rapid heating and cooling rates ensure a fine and uniform microstructure. Thirdly, the formation of lots of in-situ intermediate phases and the reservation of the un-molten strengthening phases are favorable for a higher corrosion and/or wear resistance [29,30], better thermal fatigue resistance [31], and useful magnetism properties [32]. More importantly, laser assisted surface modifications have the advantages of environmental friendly, simple, flexible, time-saving and material-saving [25]. Rolink et al. [33] compared the thermal resistance of the samples treated by thermal spraying with that by laser remelting and laser cladding. Results revealed that the laser cladding sample had the highest thermal shock resistance owing to the strong bonding between the coating and substrate.

At present, laser cladding of magnesium alloys has developed into a novel research area. This paper reviews the relevant studies in laser cladding of magnesium alloys from processing parameters optimization and cladding materials selection, summarizes the development status, puts forward the current problems and makes prospect to the future development tendency. This paper is expected to play a guiding role for the studies in this area.

2. Laser cladding process

Laser cladding is an interdisciplinary technique, which combines the laser technology, computer aided manufacturing (CAM) and the control system together [34]. Laser cladding utilizes a laser heat source to deposit a thin layer of preplaced materials on a moving substrate, as shown in Fig. 1 [35]. Moving of the substrate can be controlled through the operating system. The specimen after laser cladding is usually divided into four parts: cladding zone (CZ), interfacial zone (IZ), heated affected zone (HAZ), and the substrate (SUB) [36].

As mentioned in the *Introduction* section, good metallurgical bonding between the coating and substrate can be obtained with laser cladding technique. In order to promote the further application, more studies should be carried out in the laser cladding process on magnesium alloys. Macro morphologies, microstructures, and properties of the cladding coatings are tested and the results of them are taken as the criteria of the cladding process. And the main influencing factors on the qualities of the coating are summarized, including processing parameters, feeding ways of the material, the cladding material systems.

2.1. The processing parameters

The parameters, such as laser power, scanning velocity, beam diameter, beam focal position, are related to the cladding geometry,

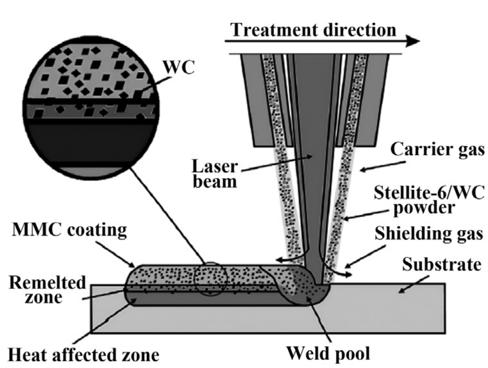

Fig. 1. The schematic diagram of laser cladding process [35].

Table 1
The phases and microstructures under different laser powers [37].

Powers (kW)	2.5	3.0	3.5	4.0
Phases	Mg_2Al_3 (fcc) + P3	P3	P3	α-Mg + P3
Structures	the petal-like phase + S3	S3	S3	the grey zone, the black massive precipitated phase

Note: P3 referred to $Mg_{17}Al_{12}$, Mg_2Si and Mg_2Al_3 (hcp) phase constitution obtained under 3.0 kW; S3 referred to the refined dendrite, needle-like and the grey zone microstructure obtained under 3.0 kW.

dilution rate, layer thickness, aspect ratio, microstructure and the mechanical properties. For example, the low melting points (~560 °C) of magnesium alloys make them liable to be melted during the laser cladding process, and then the coatings are diluted by substrates. The dilution rate values are always changing with the processing parameters [37]. To control the interactions in the molten pool and synthesize coatings which have uniform composition, dense microstructure and better properties, it is essential to adjust the processing parameters.

Gao et al. [37] revealed the influence of laser power on AZ91HP magnesium alloy during laser cladding process. The laser powers were 2.5–4.0 kW with a constant scanning velocity of 300 mm min^{-1} and a laser beam size of 10×1 mm^2. The phase constitutions and microstructures were listed in Table 1. Results illustrated that 3 kW was optimum for the wear resistance. Nevertheless, under the effect of 2.5 kW power, the precipitation of petal-like Mg_2Al_3 phase contributed to the best improvements on corrosion resistance owing to the similar electrode potential with $Mg_{17}Al_{12}$. Under higher powers, the α-Mg solid solution appeared due to the high dilution rate of magnesium, which was detrimental to the corrosion resistance of the coating.

The laser power represents the available energy that can be absorbed by the molten pool. Expect for the influence on phase composition, it affects the surface morphology meanwhile. For example, a very high power might lead to surface evaporation and crater formation. Conversely, a low power would cause inadequate melting and intermixing, leading to inhomogeneous distribution of hard particles [38].

Wang and Yue [39] studied the microstructure and corrosion resistance of the Al-Si cladding coatings fabricated with different laser scanning velocities on ZK60/SiC particle reinforced composite. The cladding coating was divided into the undiluted layer, the diffusive layer, and the interfacial layer under 8 mm s^{-1} scanning velocity. While, only diffusive layer + interfacial layer, and undiluted layer + interfacial layer appeared under the scanning velocities of 5 mm s^{-1} and 10 mm s^{-1}, respectively. Because the Al/Mg_2Si composite in the diffusive layer caused the galvanic corrosion, the corrosion resistance of the coating was not improved greatly. However, the coating treated under 10 mm s^{-1} had a structure of Al-Si eutectic and exhibited the best corrosion resistance due to the absence of Mg_2Si. The laser scanning velocity was found significantly influencing the existing time of the molten pool, the process of heat and mass transferring, the cooling rate, and as a result, the microstructure and composition of the coatings changed with different scanning velocities.

The laser beam focal position was found having non-ignorable influence on the cladding coating. Riquelme [40] researched the effect of three kinds of focus modes (negative defocus, focus, and positive defocus) in Al-SiC_p laser cladding on ZE41 magnesium alloy, as shown in Fig. 2. The optimum focus height was the second focus condition because the preplaced powders were melted by the laser beam and were not rebound away from the surface, so the interface of the coating-substrate was the best (Fig. 2(b)). Under the negative defocus condition, the powders were not completely melted and they tended to be rebound away from the surface without depositing because they never passed through the highest power zone of the beam (Fig. 2(a)). Under the

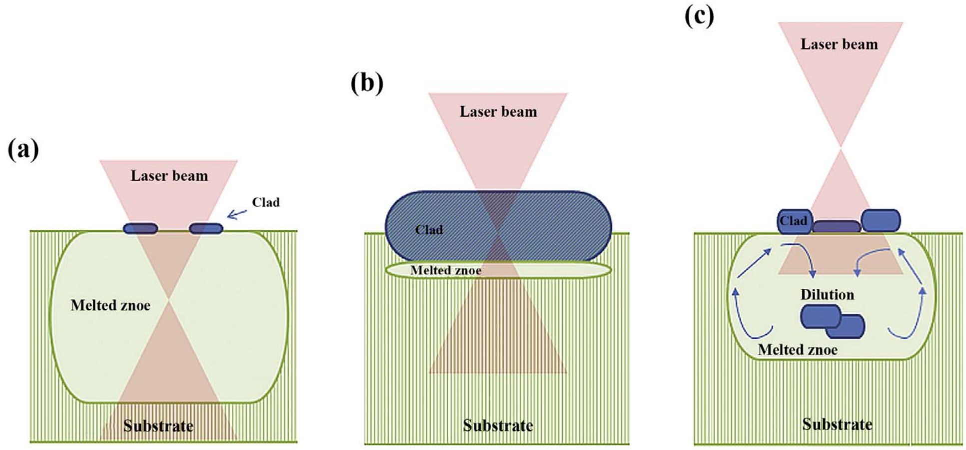

Fig. 2. Schematic of various laser beams: (a) negative defocus, (b) focus and (c) positive defocus plane [40].

positive defocus condition, a larger melted zone and a higher dilution were observed, which weakened the properties of the coating (Fig. 2(c)).

Moreover, wavelength of the laser beam has important effects on the laser absorption of metals. Different categories of laser are used to clad coatings on magnesium alloys, including CO_2 laser (10.64 µm), YA G laser (1064 nm), diode laser (848 nm), and excimer laser (248 nm). Previous investigation showed that the laser with shorter wavelength was more advantageous to be absorbed by metals [41]. Besides, the coupling effects between laser beam and the treated materials are influenced by the laser absorption rate. To clarify it clear, Ignat et al. [42] calculated the absorption rate η of 1.06 µm pulsed laser beam with Equation of $\eta = E_a/E_i$. E_a was the energy absorbed by the irradiated material, which was obtained by the isothermal differential Calvet micro-calorimeter. E_i was the incident energy of the laser beam, which could be measured by trapping the beam at a hollow sphere made in absorbing material. However, the method was very sensitive because the laser source used during the experiments must keep stable and all the pulses must be identical. Results also showed that the pretreated techniques (anodising and mordancage) had positive influences on the interactions between the laser beam and material. The calculation results were propitious to further understand the behaviors of magnesium alloys during the laser treatments.

Under the effect of laser beam, partial heats are transmitted to substrate, and then the distribution of absorbed energy between the cladding material and substrate should be noted. The energy absorbed by the substrate would lead to the melting of itself, thus a dilution zone formed under the cladding layer. The ratio of heights (Fig. 3(a)) or areas (Fig. 3(b)) is defined as the dilution rate γ, which can be calculated as follows:

$$\gamma = b/(b+h)\ {}^{[34]} \text{ or } \gamma = S_1/(S_l + S_2)^{[43]} \tag{1}$$

where b, h represent the height of the dilution zone and coating layer, respectively, and S_1, S_2 represent the area of the dilution zone and coating layer, respectively.

Ignat et al. [44] studied the relation between dilution rate and laser processing parameters, and their effects on the macro morphology and inner quality of the cladding layers were analyzed. Different dilution rates were observed on WE43 and ZE41 owing to the different thermal conductivities of the two substrates. When comparing the macrostructures of coating layer at beginning part with that of ending part, they found a higher dilution rate and lower porosity at the ending part, as shown in Fig. 3(c) and (d). In order to avoid excessive substrate heating, they controlled the laser power in the case of single-coat layer cladding and increased the processing velocities between two consecutive layers in the case of multi-coat layer cladding. Subsequently, the coating was obtained which was nearly free of pores and cracks and showed metallurgical bonding with the substrate.

Therefore, the dilution rate is related to the processing parameters (laser power, scanning velocity, beam focal position, and so on), is also affected by the substrates, coating materials and the thickness of preplaced layer [43]. Proper value of γ will guarantee not only the original performance of the coating but also the homogeneous microstructure and the metallurgical bonding between the coating and substrate [34,43].

In summary, adjustment of processing parameters relies on the optimization of laser power, scanning velocity, beam diameter, beam focal position, and so on. By having effects on the dilution rate, layer thickness, aspect ratio and others, the proper controlling of processing parameters guarantees the cladding process can be succeeded.

2.2. The feeding ways of cladding material

There are several feeding ways of cladding material, such as synchronous feeding (one-step, Fig. 4(a), (b), (c)) and preplaced coating (two-step, Fig. 4(d)) methods.

During the one-step laser cladding, deposited material can be supplied in three forms: paste feeding, powder injection, or wire feeding [34]. For example, the amorphous alloy $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ was cladded on magnesium substrate using blown powder method [45]. A shallow molten pool was created and the premixed powders were delivered into substrate at the same time. Finally, a coating with dense microstructure formed and no cracks or pores appeared on the surface. The laser beam can melt the cladding material and substrate simultaneously instead of being obstructed by the preplaced coating, especially in the process of powder injection cladding. Thus, higher quenching and cooling rates could be obtained and the process contributed to the formation of amorphous phases [34,45].

During the two-step process, the powders are preplaced on the surface of the substrate before laser irradiating. Appropriate shielding measures should be taken in order to prevent the molten pool from severe oxidation. Paital et al. [46] synthesized coatings with better corrosion and wear resistance by melting Al precursor powders on AZ31B magnesium alloy. The Al powder was sprayed on the substrate with a thickness of 200 µm before laser processing. The operation of the two-step method is simple while pores occur easily owing to the usage of the improper chemical binder in the prefabricated process. Moreover, controlling of the heat is a very important solution to prevent the high dilution rate [34].

In summary, apart from the parameters mentioned in Section 2.1, the cladding material feeding way, the preplaced coating thickness, and the powder feeding rate should be also taken into consideration during the laser cladding process. The relations among them are very intricate and more work should be conducted to renovate the

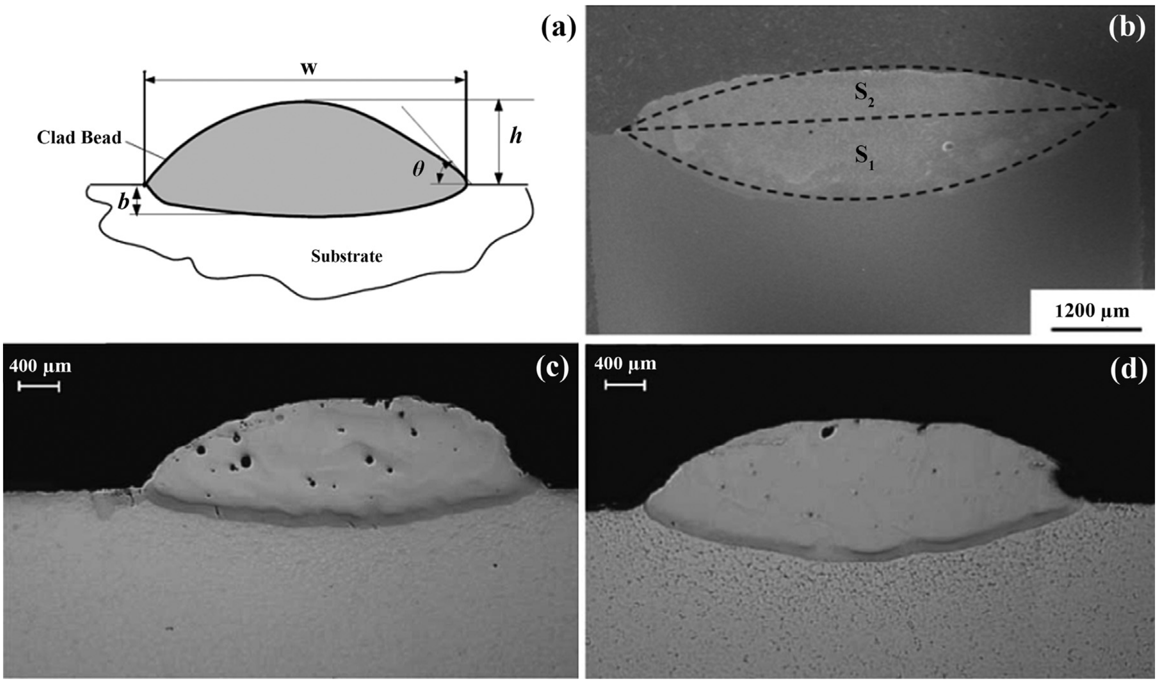

Fig. 3. A typical cross section of a clad bead (a) [34], Morphology of the cross section of the Ni-based alloy +5 wt% B_4C coating (b) [43], Macrostructure of the side injection Al powder coating of the beginning part detail (c) and the ending part detail (d) [44].

laser cladding technique.

3. Cladding material systems on magnesium alloys

Apart from the processing parameters mentioned above, the cladding materials also play an important role in controlling the microstructure and properties of the cladding coatings. Up to now, there are two kinds of alloys (homogenous and heterogeneous) used to enhance the corrosion and/or wear resistance of magnesium alloys. The "homogenous" means the cladding material has the same composition with substrate, while "heterogeneous" means different. Usually, the cladding materials should have similar physical and chemical properties (melting temperature, thermal expansion coefficient, modulus of elasticity) with the substrate to obtain coatings having dense microstructure. To maintain the same composition and properties between renovated coating and substrate, Wang et al. cladded homogenous material on the surface of magnesium part [47]. Under optimal shielding gas pressure and laser processing parameters, a dense and fine coating which had a metallurgical bonding with substrate was generated. The method had met the requirement of renovation of porosity and scuffed (or damaged) areas on the surfaces of magnesium parts. Nevertheless, the related research haven't been widely spread,

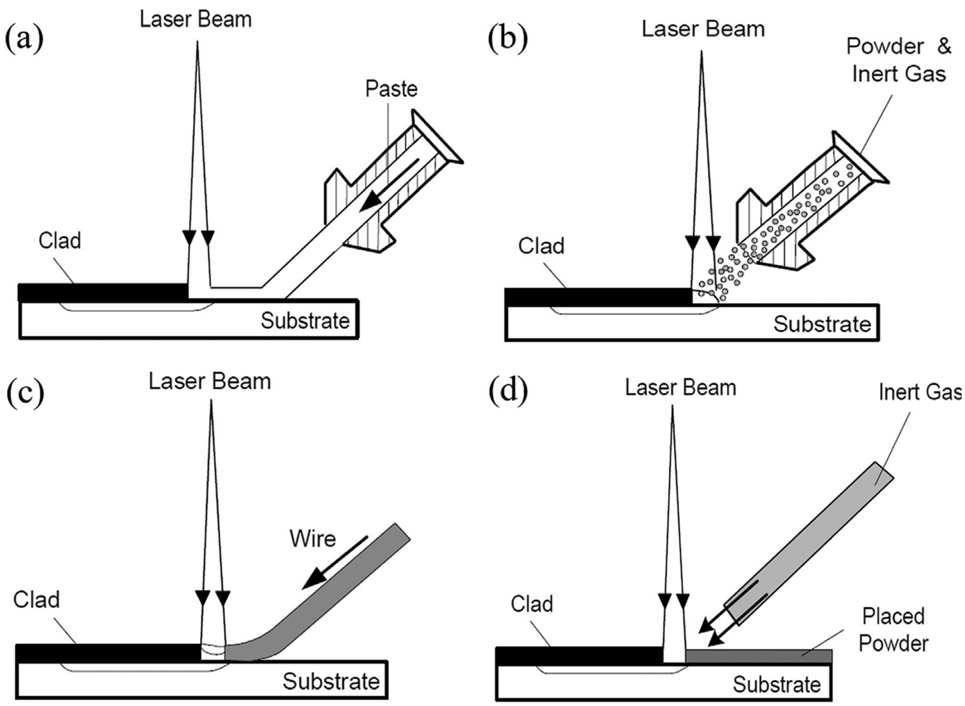

Fig. 4. Different methods of laser cladding: (a) paste feeding, (b) powder injection, (c) wire feeding and (d) preplaced powder [34].

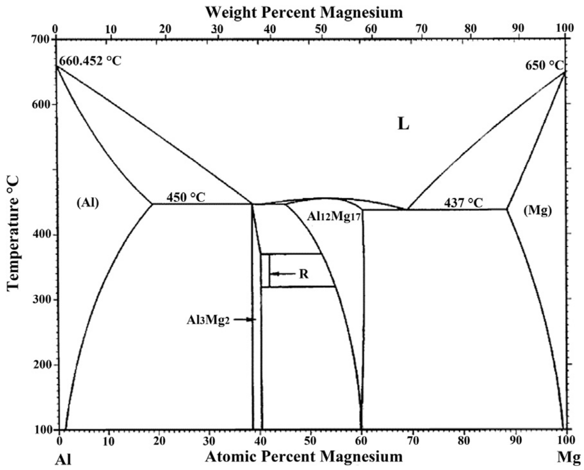

Fig. 5. Al-Mg phase diagram [54].

and the main studies concentrate on the heterogeneous cladding materials, which include pure aluminum [44], Al-based alloys [48], Fe-based alloys [49], ceramic materials [50], etc. Nowadays, the amorphous alloys [45] and HEAs [51] are catching great attention of a multitude of investigators. And the heterogeneous material systems adopted on the magnesium alloys can be divided into the following categories.

3.1. Pure metal and binary alloy coatings

Certain mechanical properties of magnesium alloys can be significantly improved by the addition of alloying elements [52]. The authors have investigated the feasibility of laser cladding on some Mg-based alloys with Al, Zr, Cu, Zn, Fe, Si and different combinations among these elements. In most cases, laser cladding process leads to an increase of hardness, corrosion and wear resistance by the comprehensive actions of all elements.

Mg-Al alloy is most widely used because Al is a well-known solid solution strengthener in Mg [53]. And some of phases formed by laser cladding can be predicted according to the equilibrium Al-Mg phase diagram [54] (Fig. 5). The in-situ synthesized hard compounds can prevent dislocations from propagating. Besides, adding Al into magnesium alloys can increase the electrode potential and form corrosion resistant coating. Hence, numerous investigations have been carried out in laser cladding on magnesium alloys with Al-based alloys.

Al-Si alloys have very little difference in the melting points with that of magnesium alloys. Therefore, many researchers devoted themselves to fabricating Al-Si coatings with finer microstructure and better mechanical properties on magnesium substrates. However, the problem of the high dilution rate still exists, making the process rather an alloying than a cladding process.

Bernabe et al. [55] fabricated coatings by laser cladding Al-Si powders on three different magnesium alloys (AZ61, ZK30 and WE54). Results showed that defect-free coatings with higher hardness, better corrosion and wear resistance were obtained. Chen [56] et al. cladded Al-Si powders on Mg-Gd-Y-Zr magnesium alloy and discussed the influence of scanning velocities on the process of laser cladding. The microstructure of the top and bottom layer at the scanning velocity of 2 mm s^{-1} were shown in Fig. 6(a) and (Fig. 6(b)), respectively. Combining the elemental distribution with the results from XRD (Fig. 7), the top layer mainly consisted of $Al_2(Gd,Y)$ (white region), $Mg_{17}Al_{12}$ and Mg eutectic (grey region, as arrowed in Fig. 6(a)), and Mg_2Si phase (black region). The coatings without apparent defects were obtained, which showed metallurgical bonding with the substrate (Fig. 6(b)). Potentiodynamic polarization curves indicated that scanning velocity played a crucial role in determining the corrosion resistance of the cladding layer, as shown in Fig. 8. Compared with the untreated Mg-Gd-Y-Zr alloy, it was obvious that the corrosion potential was increased by 0.64 V, while the corrosion current density was reduced from 2.10×10^{-5} A cm^{-2} to 1.64×10^{-6} A cm^{-2} under the scanning velocity of 2 mm s^{-1} (Fig. 8). Results showed that laser cladding with Al-Si powders was an effective way to improve the surface properties of Mg-Rare earth alloys.

Volovitch et al. [57] deposited Al-Si powders on commercial ZE41 alloy by laser cladding, and obtained three consecutive tracks under gradually increased scanning velocities. They divided the corrosion process into three stages:

a. Partial dissolution of Mg_2Si particles with formation of crevices.
b. Pitting corrosion of matrix in contact with crevices.
c. Complete matrix dissolution at later stages.

The initial corrosion was attributed to the simultaneous chemical and electrochemical dissolution of Mg_2Si. Then the matrix (the corresponding metal Al or intermetallic $Mg_{17}Al_{12}$) was corroded at the position close to the initial corrosion zone. And they indicated that the presence of different phases in the matrixes was responsible for the decrease of corrosion resistance. Thus, optimizing the processing parameters can minimize the microstructure inhomogeneity, control the area of overlap zone, avoid the formation of Mg_2Si dendrites, and it is necessary to enhance the corrosion resistance of the coatings.

The wear resistance of Al-Si cladding coatings on magnesium alloys is also investigated. Yang et al. [58] cladded Al-Si powders (with diffident weight ratio of Si) on AZ91D magnesium alloy under power density of 0.783×10^9 W m^{-2}. When Si content was 8.0 wt%, a small amount of Mg_2Si phase formed. When Si content in the mixed powders was 60 wt%, except for the substantial amount of Mg_2Si, a slight of

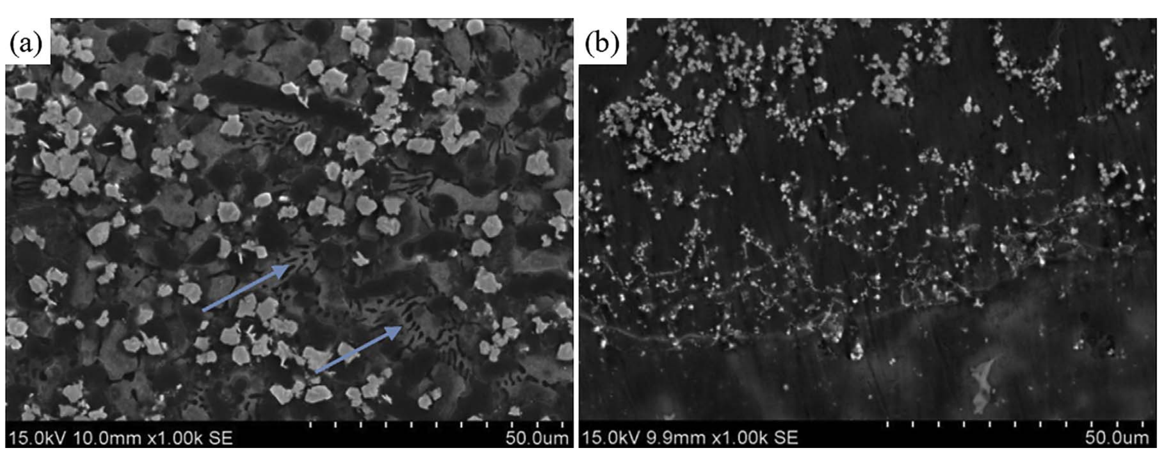

Fig. 6. Microstructures of the cladding layer at the scanning velocity of 2 mm s^{-1}: (a) top zone and (b) bottom zone [56].

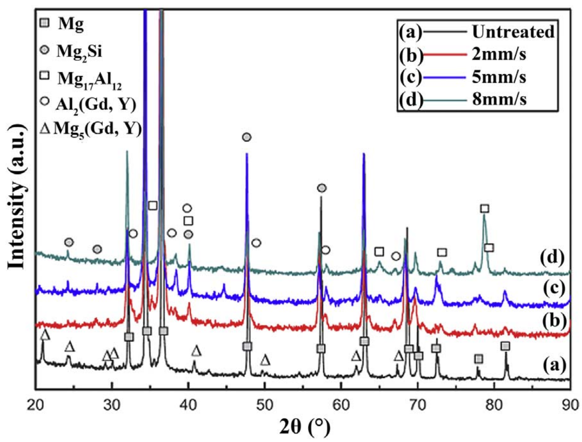

Fig. 7. XRD patterns of untreated and laser cladded Mg-Gd-Y-Zr alloy samples at different scanning velocities [56].

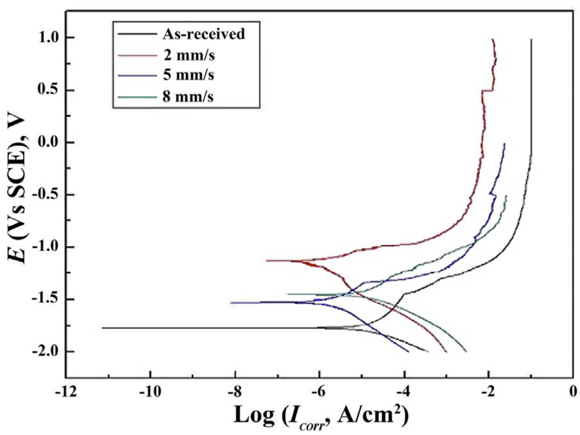

Fig. 8. Potentiodynamic polarization curves of the untreated and laser cladded Mg-Gd-Y-Zr alloy samples at different scanning velocities [56].

dendrite $Mg_{17}Al_{12}$ was synthesized by the reaction between Al and Mg. And when the cladding material was Al-12.5 wt% Si eutectic alloy powder, a relatively uniform distribution of Mg_2Si phase in the fine dendrite of $Mg_{17}Al_{12}$ was observed. Results of wear test of the cladding layer and substrate were shown in Fig. 9. It was noticeable that the layer fabricated with 12.5 wt% Si exhibited the best wear resistance, which was attributed to the uniformly distributed Mg_2Si and the presence of fine $Mg_{17}Al_{12}$ compounds.

Fabre et al. [59] studied the effect of laser surface alloying on the wear resistance of ZE41 magnesium alloy with Al-12 wt% Si powders. Before Al-Si powders were deposited on ZE41-T5 substrate, the conversion treatment was applied to obtain better coupling efficiency between the laser beam and substrate. Mg_2Al_3, $Mg_{17}Al_{12}$, Mg_2Si and Al-rare earth phases were detected from the bottom to top of the coating. Results showed that the hardness and wear resistance of the alloy were significantly enhanced after laser treatment.

Yue et al. [60] added the Al-Si eutectic alloy on the ZK60/SiC magnesium alloy using a multiwave Nd: YAG laser. Results indicated that laser cladding coatings had tight interface bonding and had not major defects within a narrow range of operating window. While, a high dilution rate of the coating appeared due to the high diffusion coefficient of the molten magnesium in Al-Si alloy, which had a detrimental effect on the corrosion resistance.

Qian et al. [61] solved the high dilution rate of substrate and obtained excellent results. A 6 kW CO_2 laser was used to remelt the plasma sprayed Al-12 wt% Si coating on the surface of AZ91D magnesium alloy. A homogenized laser beam was performed for

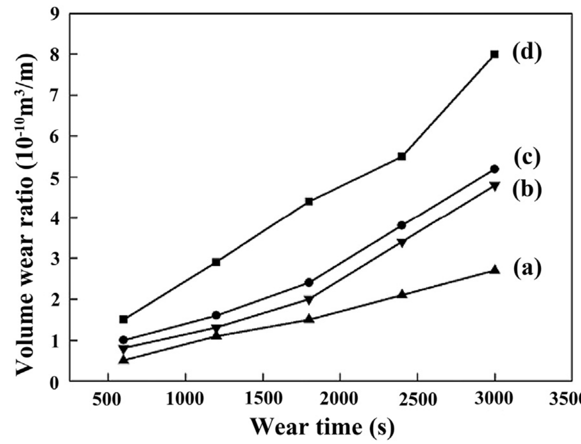

Fig. 9. Comparison of wear loss of laser treated samples with different Si content in the mixed powders: (a) 12.5 wt%, (b) 60 wt%, (c) 8 wt% and (d) as-received magnesium alloy (all under the condition of scanning velocity $1.5\ mm\ s^{-1}$, power density $0.783\times10^{9}\ W\ m^{-2}$) [58].

minimal dilution and the laser remelted coating was composed of fine primary α-Al dendrites and Al-Si eutectic matrix. Because the Al-Si coating was not affected by the dilution from substrate, the Mg_2Si phase did not appear. Combining the electronegative eutectic with dense network microstructure, the laser remelted coating showed a better corrosion resistance.

Obviously, the appearance of Mg_2Si phase contributes to the improvements of hardness and wear resistance, while it is not beneficial to the corrosion resistance owing to its action in the initial corrosion stage. Investigations identify that eutectic structures are helpful to the excellent properties. Besides, forming uniform microstructure and controlling the proper dilution rate are severe issues which can improve the corrosion resistance of the cladding coating.

Other Al-based powders are also used, such as Al-Cu, Al-Zn, Al-Mg, etc. Gao et al. [62] fabricated Al-Cu coatings on AZ91HP magnesium alloy by broad-beam laser cladding. And the cladding layer was characterized by $AlCu_4$ and $Mg_{17}Al_{12}$ grains, being embedded in an Al-Mg matrix. The occurrence of multiple intermetallic compounds in the coating contributed to the enhancement of the corrosion and wear resistance of AZ91HP magnesium alloy. The laser cladding of preplaced Al + Ir powders were performed on the ZM5 magnesium alloy by Chen et al. [63]. And they obtained a cladding layer with AlIr, $Mg_{17}Al_{12}$ and other Al-based phases, which were beneficial to the corrosion resistance of magnesium alloy. Mei et al. [64] studied the effect of Al-Zn powders on the corrosion resistance of ZK60/SiC composite by laser cladding. Results showed the laser cladding sample dominated the most fine and homogeneous microstructure, and the method was an effective way to improve the corrosion resistance of Mg-based metal matrix composite. Wang et al. [53] fabricated both magnesium-rich ($Mg_{53}Al_{47}$ and $Mg_{72}Al_{28}$) and aluminum-rich ($Mg_{27}Al_{73}$) coatings by laser cladding, and the problems of high vapor pressure and being oxidized easily had been overcome according to the adapted apparatus and technique.

Apart from the Al-based alloy powders, other alloys were also used to realize surface modification of magnesium alloys. Yue et al. [49] fabricated a stainless steel layer on ZK60/SiC composite through a two-step method (thermal spraying and laser remelting) using brass and copper as interlayer. Though the corrosion resistance was enhanced, there still existed some space for its improvement because of the galvanic corrosion between copper (lower potential position) and stainless steel (higher potential position) in seawater. The corrosion attack at the copper-rich spheroid was shown in Fig. 10. The laser cladding sample did not show a passive region in the polarization plot due to the segregation of copper-rich phase at the interdendritic regions and the presence of copper-rich spheroids in the stainless steel matrix. Therefore, it should be noted that the addition of interlayer promotes

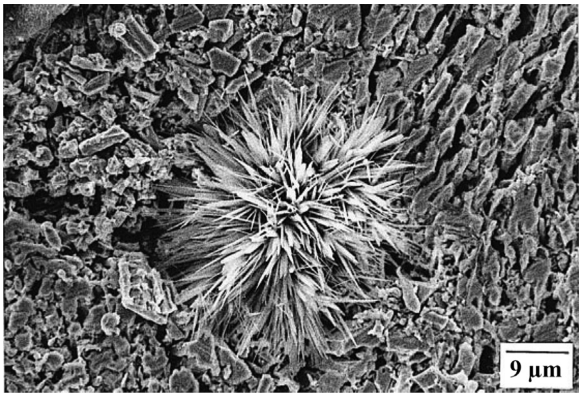

Fig. 10. Corrosion attack at a copper-rich spheroid [49].

the metallurgical bonding between the coating and magnesium matrix, meanwhile it also brings in some adverse effects on the corrosion resistance. It is important to consider whether the galvanic cells will form among different phases when choosing interlayer materials.

Subramanian et al. [65] cladded Mg and Zr mixed powders onto AZ91B magnesium alloy. The cladding coatings showed homogeneous microstructure with martensitic characteristics (hcp). Results demonstrated that Zr was another beneficial element to improve the corrosion resistance of magnesium alloys.

Al-based alloys have been developed sufficiently, and other traditional metallic coatings (such as Zr-based, Cu-based, Ni-based etc.) should be also paid more attention to overcome the difficulties met in the laser cladding process.

3.2. Multi-element alloy coatings

3.2.1. Ternary alloy coatings

Due to the low melting points and high coefficient of thermal expansion [6] (shown in Table 2) of magnesium alloys, it is difficult to choose a proper cladding material to avoid forming cracks and the high dilution rates. The appearance of certain ternary alloys supplies an opportunity to solve the relative problems. The ternary alloys designed according to the cluster line criterion (refers to a specific composition line linking a specific binary cluster composition to the third element, which reflects the structure relationship between the optimized ternary alloy and the basic binary cluster) have good compatibility, better bonding capacity with magnesium alloys, excellent mechanical and chemical properties [66].

Wang et al. [66] designed Ni-Zr-Al alloys and cladded them on AZ91HP magnesium alloy. The composition relationship between the special cluster and the third element Al was shown in Fig. 11(a). After comparing the melting temperature, microhardness, corrosion rate among the $(Ni_{0.64}Zr_{0.36})_{100-x}Al_x$ alloys, the $Ni_{60.16}Zr_{33.84}Al_{6.0}$ alloy was chosen and used for cladding material ultimately. Owing to the high heating and cooling rates during the cladding process, an amorphous phase and two ternary intermetallic phases ($Ni_{10}Zr_7$ and $Ni_{21}Zr_8$ types) were synthesized and distributed homogeneously in the matrix. The improvements on microhardness and corrosion resistance were respectively depicted in Fig. 11(b) and (c). The mechanical properties were similarly enhanced when cladding Ti-Ni-Al alloy on the surface of AZ91HP, while it was different that only β-Ti solid solution and Ti_2Ni intermetallic compound were found, amorphous phases were not observed in the coating [67].

The cladding coatings fabricated with the designed ternary alloys will bond tightly with substrates, because the designed materials possess very good adaptability to the substrates and the laser cladding process, which avoid the formation of surface defects, burning loss and excessive dilution of substrates. Owing to the synthesis of various intermetallic and amorphous phases, the coatings with excellent properties can be obtained after laser cladding. So many superiorities make it essential to further develop the ternary alloy systems to realize wider applications of laser cladding on magnesium alloys.

Table 2
Physical properties of Mg, Al, and Fe [6].

Property	Magnesium	Aluminum	Iron
Crystal structure	Hcp	Fcc	Bcc
Density at 20 °C (g/cm^3)	1.74	2.70	7.86
Coefficient of thermal expansion 20–100 °C ($\times 10^6$/°C)	25.2	23.6	11.7
Elastic modulus [Young's modulus of elasticity] (10^6 Mpa)	44.126	68.947	206.842
Tensile strength (Mpa)	240 (for AZ91D)	320 (for A380)	350
Melting point (°C)	650	660	1536

3.2.2. Amorphous alloy coatings

Amorphous alloy has short-range order and long-range disorder arrangement, so it has distinctive properties including excellent ductility of metals and stability of ceramics [68–70]. When the characteristics of amorphous alloys were discovered, the Ni-Cr-P-B amorphous alloys were laser cladded on some mild steel by Yoshioka et al. [71]. Several years later, Zhu et al. [72] fabricated $Fe_{38}Ni_{30}Si_{16}B_{14}V_2$ amorphous composite coating on AISI 1045 steel by laser cladding in order to increase the wear resistance.

Nowadays, amorphous materials have been used for laser cladding on magnesium alloys. Laser cladding of Cu-based amorphous alloy and SiC reinforced composite on magnesium substrate was conducted by Huang et al. [73,74] using the preplaced laser processing method. Owing to the higher laser absorptivity of SiC, the following reaction might occur in the molten pool:

$$SiC \rightarrow Si + C\ (T > 1650\ ^\circ C) \tag{2}$$

The Si and C atoms enlarged the glass forming ability (GFA) of the matrix and formed several silicide and carbide compounds through reacting with other elements, which greatly improved the hardness and wear resistance of the coating.

Yue et al. [45] investigated the corrosion and wear properties of laser cladding $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ amorphous coatings on magnesium alloy using the blown powder method. A 1.5 mm coating was fabricated with an amorphous structure up to the depth of 1.1 mm. The wear resistance of the coated specimen was proved to be thirteen times higher than that of the substrate, and the corrosion current decreased by three orders of magnitude.

Considering the ductility of the monolithic amorphous alloy was low, Yue et al. [75] fabricated $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ amorphous coating using multiple-layer laser cladding. The coating exhibited a graded microstructure characteristic: amorphous structure (at the top, Fig. 12(a)), amorphous-nanocrystalline structure (in the middle, Fig. 12(b)), predominant crystalline structure (at the bottom, Fig. 12(c)). The formation of the amorphous-nanocrystalline composites were considered to be due to the reheating effect. The crystalline phases were changed from the amorphous layer induced by the reheating during the cladding of subsequent layers. The average wear volumetric loss of the magnesium substrate, the full amorphous coating and the amorphous-nanocrystalline composite coating were presented in Table 3. In terms of the results of wear test, the wear resistance of the amorphous-nanocrystalline composite was 16 times higher than that of the substrate and was slightly higher than that of the full amorphous alloy, which showed the nanocrystals improved the wear resistance of the amorphous alloy. When SiC particles [76] were added in $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ amorphous on magnesium alloys, monolithic amorphous phases disappeared in the coating. The wear resistance of the coating was improved, while the corrosion resistance was inferior because

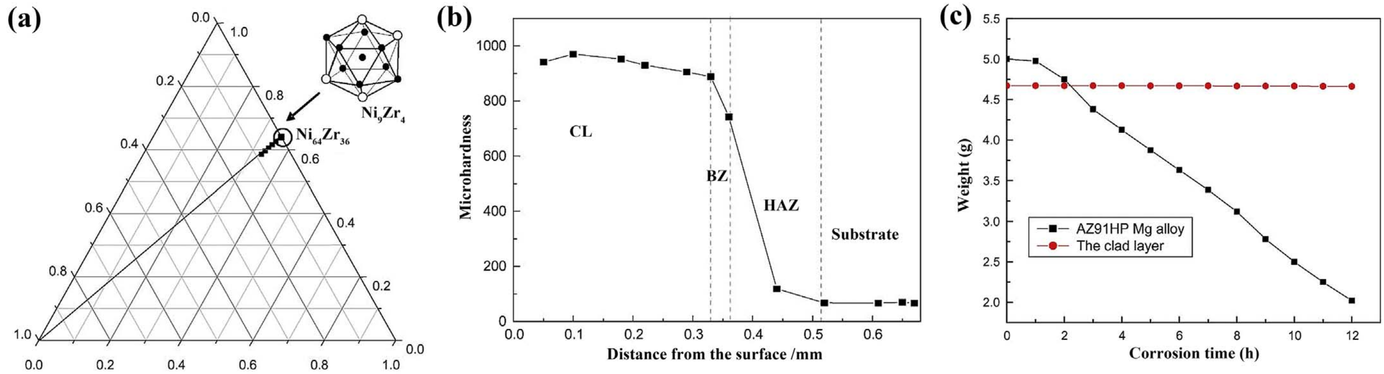

Fig. 11. (a) Composition chart of the Ni-Zr-Al system, (b) Microhardness plot along the cross-section of the coating, (c) The corrosion curves of the cladding layer and AZ91HP Mg alloy [66].

SiC particles disturbed the continuity and integrity of the passive Zr-oxide film.

Therefore, combining amorphous alloys with other strengthening particles and forming variously mixed homogeneous microstructures are beneficial to improve the corrosion and wear resistance of the cladding coatings.

Table 3
Average volumetric losses measured after a wear test time of 1 h [75].

Specimen	Average volumetric loss ($\times 10^{-3}$ mm^3)
Substrate	83.4
Amorphous	6.1
Amorphous-nanocrystalline composite	5.3

3.2.3. High entropy alloy coatings

In recent years, high entropy alloy (HEA) has become a promising material system since it was explored by Yeh et al. [77]. It is a new approach to design alloys with multiple elements in equimolar or near-equimolar ratios, which breaks through the traditional principles. The HEA has simple microstructure such as face centered cubic (FCC) or body centered cubic (BCC), which is constituted by at least five principal elements with the concentration of each element being between 5 and 35 at% [78]. During the laser cladding process, the reactions in the molten pool can be restricted owing to the high mixing entropy between the HEA constituent elements and substrate elements. Nowadays, HEA has been used for laser cladding on magnesium alloys [51] apart from steels [79,80].

Meng et al. [79–81] fabricated AlCoCrCuFeNi particle reinforced coating onto AZ91D magnesium alloy using laser melt injection (LMI) technique in an argon gas atmosphere. The morphologies of the AlCoCrCuFeNi particles after laser treatment were summarized as the following: undissolved, surface slightly dissolved, and surface seriously dissolved. It was found that the wear volume loss of the metal matrix composites (MMCs) coating was the least when the volume fraction of the HEA particles reached about 0.4. The wear surface morphologies of AZ91D, MMC (0.1) and MMC (0.4) were shown in Fig. 13. The EDS results indicated that there existed relatively serious oxidation on the wear surface of AZ91D and MMC (0.1). And the formation of cracks prompted the development of the oxide layer, which increased the oxidation-controlled wear behaviors on both of them (Fig. 13(a) and (b)). While the debris wore off from particles in the MMC (0.4) were confirmed without significant oxidation, and they underwent delamination wear (Fig. 13(c)). Results showed the friction coefficient was increased and the wear volume loss was reduced for the MMC (0.4) coating.

Yue et al. [51] fabricated the AlCoCrCuFeNi HEA coating on pure magnesium by means of laser cladding using a direct blown powder method. To overcome the big difference in melting points between the HEA powders and magnesium substrate, the HEA powders were preheated and injected into the molten pool, which formed the suspension containing aggregates of the HEA powders and increased the absorbability of the laser irradiation. The cladding coating was composed of a top HEA layer and a bottom composite layer. Through the analysis of EDS and the calculation of mixing Gibbs free energy, the composition of the HEA alloy was largely preserved and a very small dilution except for some Cu diffusing into the magnesium was observed, which ensured the excellent corrosion resistance of the coating.

The coating with excellent properties can be obtained by cladding with HEA powders, which has broad application prospects in surface modification of magnesium alloys. However, too little dilution rate is not beneficial to the metallurgical bonding between the coating and substrate. Thus, it is necessary to optimize the laser processing parameters to ensure a proper dilution rate. Meanwhile, the problems

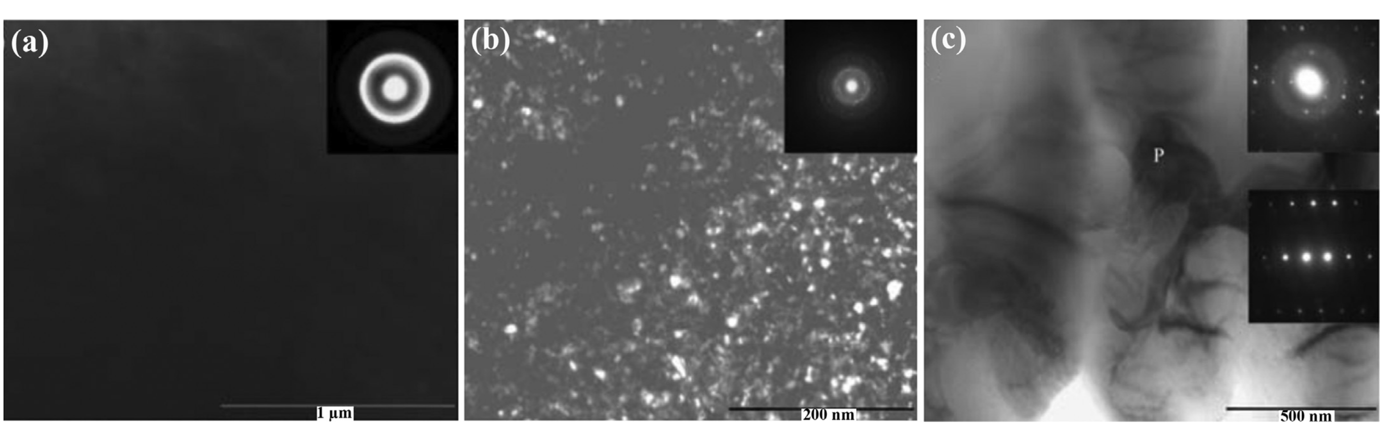

Fig. 12. TEM images and SAED patterns of the cladding coating: (a) top region, (b) middle region and (c) bottom region [75].

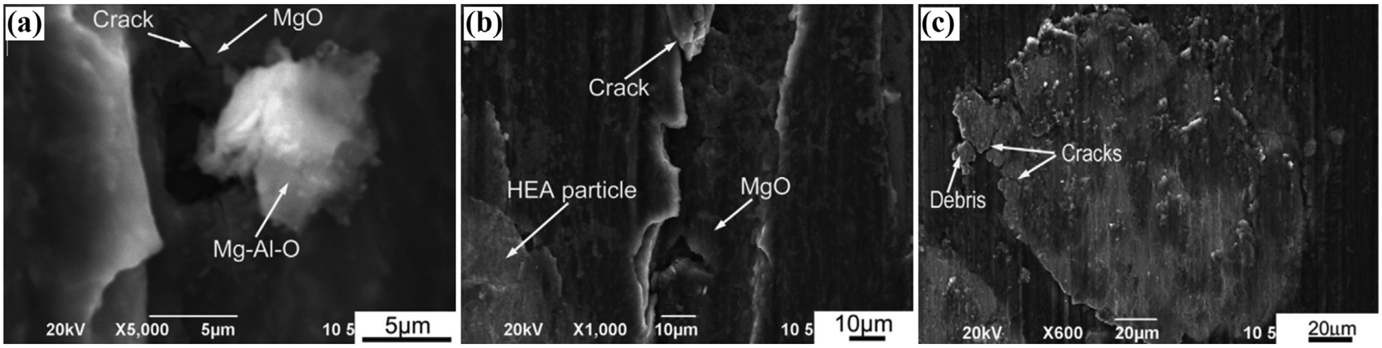

Fig. 13. SEM images of the wear surface: (a) AZ91D, (b) MMC (0.1), and (c) MMC (0.4) [81].

involved to the melting points of HEA powders and magnesium alloys should be also concerned.

3.3. Composite coatings

There also exist some cladding materials which are composed of intermetallic and ceramic powders, or sometimes a mixture of metal and ceramic. Usually, the intermetallics or metals (such as Al-Si [50], NiAl [82], and Al [83]) act as the transition phases, and they bond the ceramic phases with substrates tightly by decreasing the interfacial stress caused by the difference of physical and chemical properties between them. The ceramics, with high hardness, excellent corrosion and wear resistance and high-temperature oxidation resistance, will stay intact or partially be melted, which increases the corresponding properties of magnesium alloys. Some studies have been carried out based on the theory mentioned above.

Al + SiC powders were cladded on AZ91D magnesium alloy with a pulsed laser (Nd: YAG) by Zheng et al. [83]. The cladding coating consisted of SiC particles and intermetallic phases like $Mg_{17}Al_{12}$, filled with α-Mg and Al phase in interspaces. Owing to the high melting temperature (2300 °C), the SiC particles stayed un-molten and then were gathered to the boundaries of the previous formed cellular and dendritic structure by the internal convection, forming a network-like structure. The hardness and the wear resistance enhanced with the increase of SiC content (from 10 to 30 wt%). However, when the addition of SiC reached 40 wt%, the wear resistance begun to degrade because SiC particles were difficult to be packed by Mg-Al matrix due to the insufficient Al. Obviously, single SiC particles in the magnesium matrix are easier to cause poor interfacial strength. Only the SiC particles distribute uniformly and are embedded tightly in the matrix can the wear resistance of the coatings be improved.

Another common ceramic phase used in the process of laser cladding on magnesium alloys is Al_2O_3, and the pure Al [84,85], Al-Si [50] and NiAl [82] alloys are used as transition materials. Al + Al_2O_3 powders were fabricated on MRI 153 M magnesium alloy using a pulsed Nd: YAG laser by Samant et al. [84]. According to experimental observation and the results of thermal modeling, they found that the laser scanning velocity had an influence on the average melted depth and the amount of retained and/or reconstituted alumina in the final coating. A refined coating was obtained under optimal processing parameters, and the wear resistance of the coating zone was improved. Liu et al. [85] analyzed the influence of powder weight ratio on the process of laser cladding on AZ91D magnesium alloy. Results showed that relatively more Al_2O_3 particles and $Al_{12}Mg_{17}$ phase were obtained in the cladding coating with Al and Al_2O_3 in ratio of 3:1, which showed the highest hardness and best wear resistance.

Gao et al. [50] fabricated Al_2O_3 reinforced coatings on the AZ91HP substrate with Al-Si alloy as the transition layer. A 5 kW continuous wave CO_2 laser processing system was used to remelt the plasma spraying coating. The Al-Si alloy bonded the substrate and coating tightly, and the multi-layer microstructure was shown in Fig. 14(a). The formation of the dense column-like (Fig. 14(b)) and flock-like (Fig. 14(c)) microstructure in the coating was in favor of the superior properties than that of the substrate and plasma-sprayed coating. Qian et al. [82] induced NiAl as the transition layer for the plasma-sprayed Al_2O_3 coating before laser cladding, indicating that the bonding zone was defect-free and the wear resistance was improved in some extent.

Nowadays, addition of composite materials aims at improving the wear resistance of magnesium alloys, and the transition layer is required to bond the coating with substrate. The formation of multi-layer microstructure contributes to the improvement of the wear resistance. The optimization of processing parameters and the proper ratio of composite powders will lead to the best cladding coating. While, corrosion resistance of the composite coating is seldom researched, so more efforts should be devoted to realize its enhancement.

3.4. Rare earth elements added coatings

With large atomic radius and strong chemical activities, rare earth elements can react easily with many other elements, showing large capacities in refining the microstructure and improving the properties of alloys [86]. Padekar et al. [87] found the rare earth containing EV31A magnesium alloy had better stress corrosion resistance than Al-containing AZ91 because of the protective robust oxide/hydroxide layer formed on the substrate. In addition, the rare earth materials were widely used in metallurgy [88,89]. During the process of laser cladding, the rare earth oxides were liable to absorb more laser energy, and improved the weldability of the deposited metals on substrates [90]. Some authors studied the effect of nano-CeO_2 [91], nano-Y_2O_3 [92], Y_2O_3 [93], or CeO_2 and La_2O_3 [86] on laser cladding of Ni-based superalloy, Ti-6Al-4V alloy or steel, respectively. Coatings with better properties were obtained when certain content of rare earth oxides were added.

Effects of rare earth elements on the laser cladding process of magnesium alloys have been also researched. Zhu et al. [94] analyzed the influence of different amount of rare earths on the low power laser cladding Al-Cu alloy coatings on magnesium alloy. Thickness of the coating was increased, and the microstructure and mechanical properties were improved when Y_2O_3 powders were added. With more Y_2O_3 content, the morphologies of the crystals changed from lenticular into coarse dendritic, or fringe, or dispersed particles. These improvements might rely on:

a. Rare earth elements, which had a higher laser absorption rate, could reduce the evaporation of powders and increase the molten depth.
b. Y_2O_3 (with higher melting point) solidified earlier than Al and Cu (with lower melting points), and acted as the nucleating centers for dendrites and prevented the dendrites from coarsening.
c. Y decomposed from Y_2O_3 tended to distribute in the liquid-solid interfaces or at the grain boundaries, increasing the extent of composition undercooling and the nucleation rate, as a result the grains were refined.

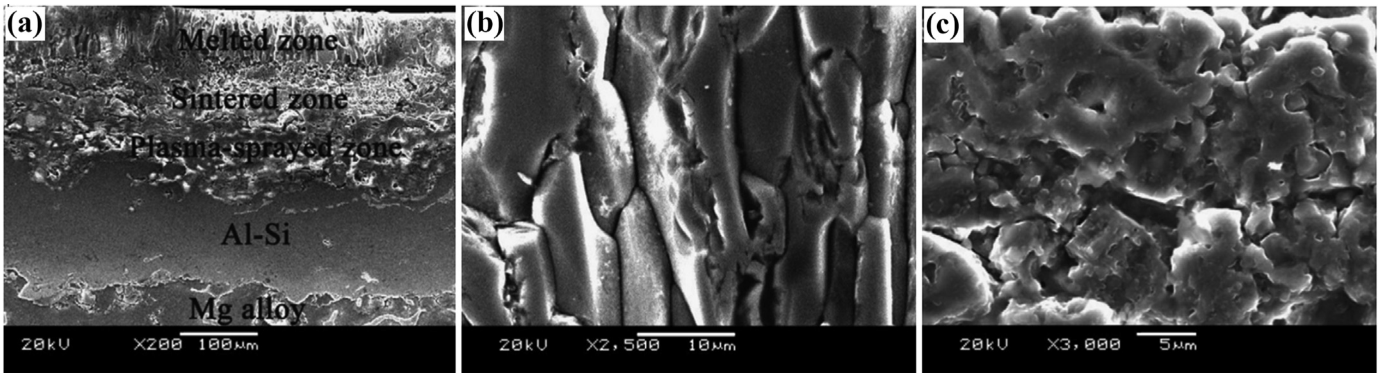

Fig. 14. Morphology of the laser cladding coating (a), Microstructure of the melted zone (b) and the sintered zone (c) [50].

d. Y could react easily with O, N, etc. elements to form stable compounds, purifying and compacting the cladding layer.

The rare earth elements can refine the microstructure, increase the laser absorption rate and activate the actions in the molten pool. The cladding coatings have better corrosion and wear resistance when the rare earth elements are added. However, the category of rare earth elements used for laser cladding on magnesium alloys is very little and the range of addition content is in a very narrow window. Thus, it is essential that cooperating laser cladding with other assisted methods or adjusting the processing parameters to extend the available range of rare earth elements.

4. Application and development tendency

4.1. The application range

Most of researches are principally aimed at improving the corrosion and wear resistance of magnesium alloys. Except for that, laser cladding treatment can be also used to repair magnesium parts, realizing the environmental and economic purpose.

4.1.1. Improvement of the corrosion and wear resistance

Relevant investigations have proven that magnesium alloys parts are vulnerable to galvanic corrosion when contacted with other materials and are easier to be worn out owing to the poor wear resistance. Researches have shown that the corrosion resistance of AZ series magnesium alloys is greatly influenced by the microstructure and the quantity and distribution of the second phases. The corrosion is caused by the great potential difference formed within the bulk metallic materials owing to the non-uniform composition, uneven structure and stress [95]. The homogeneous microstructure, grain refinement and addition of alloying elements were beneficial to alleviate above problems [96]. Laser cladding on magnesium alloys supplies such an opportunity to form intermetallic phases and obtain compact coatings on the substrate, which are in favor of improving the corrosion and wear resistance and expand their application ranges.

From the prospective of laser cladding material systems, the pure metal, binary alloys, and rare earth elements can improve both the corrosion and wear resistance, due to the formation of defect-free coatings, the uniform distribution of eutectic phases and the interaction of various phases. Though the common Mg_2Si phase is not beneficial to the improvement of corrosion resistance, the results may be different when the quantity of Mg_2Si phase reaches a certain amount. It was identified that the amount and distribution of some intermetallic phases (e.g. the β phase, i.e. $Mg_{17}Al_{12}$) could improve the corrosion resistance of the coating [97]. Ceramic particles usually contribute to enhance the hardness and wear resistance. The comprehensive actions among the constituent elements of multicomponent alloys (amorphous alloys and HEAs) play an important role in improving the corrosion and wear resistance.

4.1.2. Repair of magnesium alloys

The feasibility of depositing variable thickness of cladding material on the substrate makes it possible to repair machine parts using the method of laser cladding [98]. As a near-net-shape technique, laser processing not only helps producing component with a geometry which is close to the final dimensions, but also obtains a microstructure closing to the original one. The purpose of repairing approach is to obtain superior appearance and performance than the original on the damaged work pieces.

Compared with the conventional repair process, laser cladding has the potential to avoid the previous shortcomings such as large HAZ, high residual stresses, and so on [99]. Repair of the magnesium alloy parts by laser cladding is an advantageous solution in terms of performance requirement, as well as time-saving and cost-saving. And the feeding way of cladding materials for such purpose mainly includes synchronous powder or wire feeding.

Cao et al. [99] used laser cladding to repair ZE41A-T5 magnesium aerospace parts, and they chose a filler wire which had similar composition to the base material as cladding material. However, as shown in Fig. 15(b), the overlap defect was present at the bead spacing of 1.50 mm, which initiated cracks (Fig. 15(c)) because the surface overlaps made no bonding with the base metal. To avoid such defects, the bead spacing and defocusing distance were optimized and the operating window was proposed in Fig. 15(a). Four zones were included in Fig. 15(a). A bead spacing above 3.0 mm led to the formation of single isolated beads. Too high elevated defocusing distance might cause defects such as lack of bonding. Surface cracks formed under too low bead spacing and the elevated defocusing distance. The cladding zone indicated in Fig. 15(a) presented the optimized parameters during the single layer cladding. Apparently, introduction of the elevated defocusing distance significantly expanded the operating window. And further researches indicated that the operating window shown in Fig. 15(a) could be used to determine the layer spacing during the multi-layer cladding without defects (Fig. 15(d)). This study provided a basis for the repair of aerospace magnesium alloy components.

Capello et al. [100] used the laser cladding by wire (LCW) process to repair the sintered tools. They indicated that wires of small diameter could be used because the laser beam could be easily focused on a small area. Furthermore, complex shape, small and localized geometries such as borders, intricate profiles and pockets, could be repaired. Laser cladding on damaged magnesium parts may have a wide application to achieve the high utilization rate of magnesium alloys in the future.

4.2. Current problems

Although laser cladding technique has achieved some progress in the field of surface strengthening and modification, there still exist

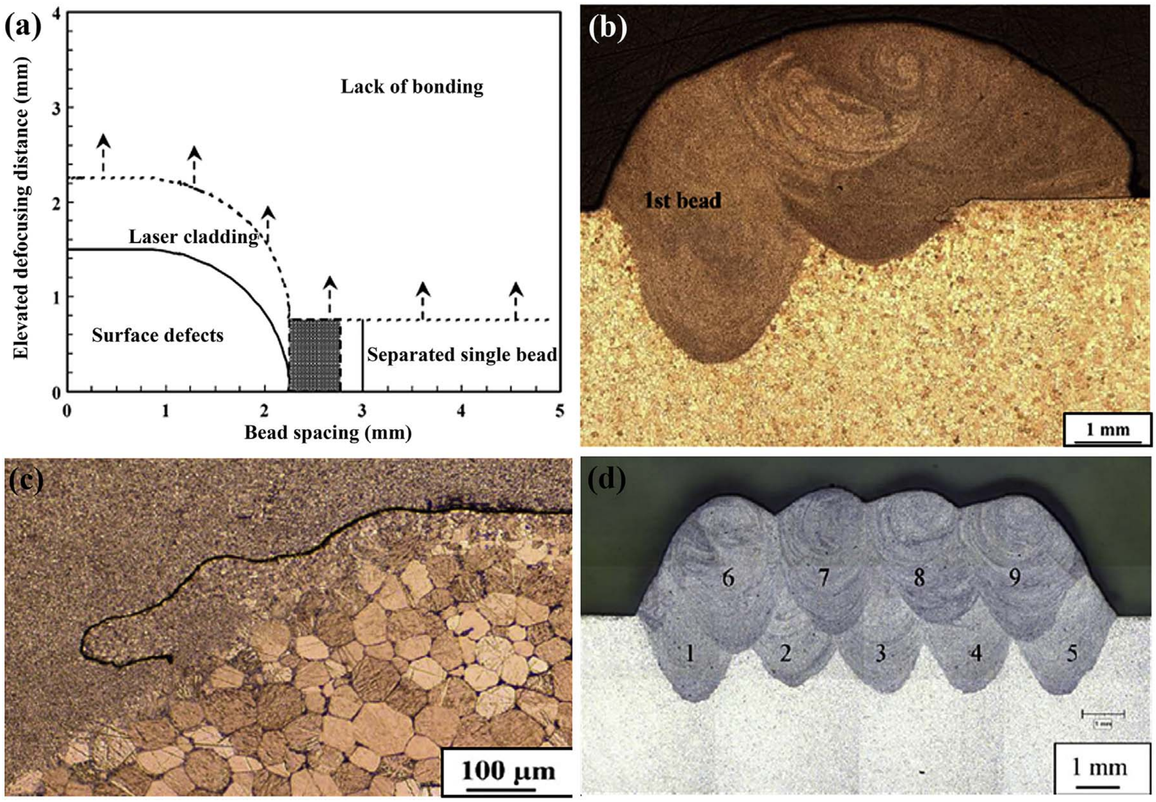

Fig. 15. (a) Laser cladding operating window for the bead spacing and the elevated defocusing distance, (b) Effect of bead spacing on the transverse shape of the double beads, (c) Optical images showing the close-up views of the crack defects in (b), (d) Surface morphology and transverse sectional shape of a two-layer cladding [99].

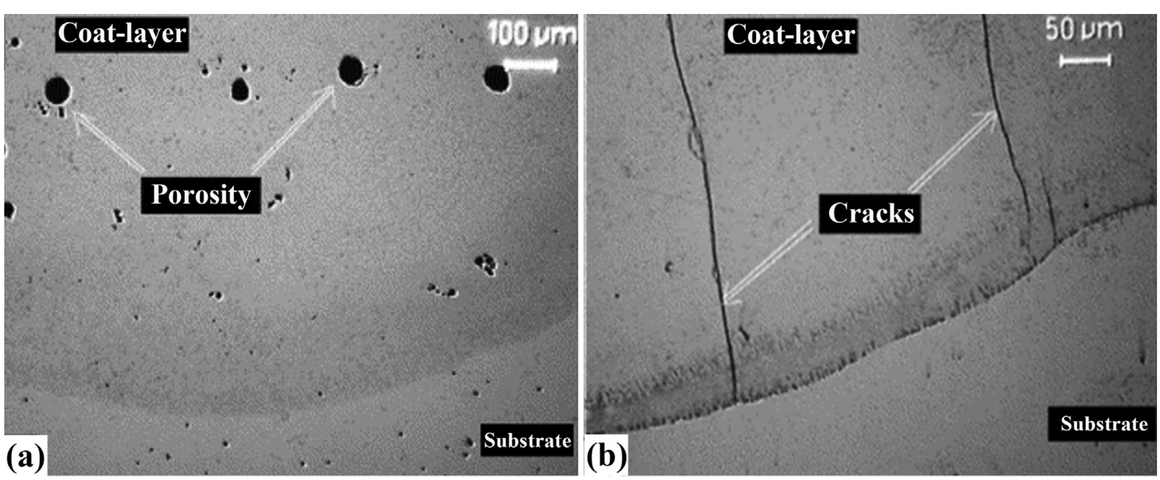

Fig. 16. Interface microstructure of the WE43-T2 laser cladded with Al powder: (a) pores and (b) cracks [44].

some urgent problems to be solved. The laser parameters, cladding materials and substrates all have vital influence on the quality of the coating on magnesium alloys. During laser cladding, the vaporization of substrate occurred and the gases could not leave the deep molten pool during solidification and was trapped inside the coating. Thus, the pores formed in the coating, as presented in Fig. 16(a) [44]. Besides, at the beginning part of the coating layer, pores were easier to form due to the rapid solidification rate and the reduced molten pool volume. On the other hand, the high stress level led to the formation of cracks, as observed in Fig. 16(b) [44]. Yao et al. [38] also observed the surface crater cracks owing to the high stress level inside the cladding layer, which could be affected by the laser powers.

The solutions to these problems (pores and cracks) should rely on improving the cladding strategies [101], optimizing the processing parameters [40], perfecting the material systems [102], and adding the transition layer [82]. It was noteworthy that the relation of laser parameters (laser power, spot diameter and scanning velocity) and laser cladding cracks was revealed by theory and experiment, which was beneficial to solve the mentioned problems [103].

Apart from pores and cracks, the laser cladding process on magnesium alloys has its peculiar shortcomings. In order to reduce the defects in laser cladding coating, proper cladding materials should be selected, which has been discussed in the third section of the paper. Here, only the problems attached to the substrate are listed.

As previously mentioned, magnesium alloys are prone to be oxidized and have high vapor pressure. In order to prevent the oxidization of the molten pool, shielding gas such as Ar should be adopted indispensably [104]. Besides, laser parameters should be optimized to overcome the high dilution rate of magnesium alloys, realizing metallurgical bonding between the coatings and substrates, and guaranteeing the excellent properties of cladding materials. For example, when the thermal conductivity of the substrate was decreased, it would retain more absorbed energy into itself and then the dilution rate of the substrate increased [44]. On the other hand, improving the laser absorption rate of magnesium alloys is a hot research topic. Some authors presented that using laser with a shorter wavelength [105], heating the substrate before cladding [106], and adding activators [107] on the surface of the substrate can increase the laser absorptivity.

4.3. Development tendency

4.3.1. Novel cladding materials

Cladding material plays a vital role in laser cladding process. Owing to the issues existing in the traditional cladding materials, more and more studies have been carried out about the novel cladding materials. Certain principles should be obeyed when the materials are designed. Firstly, good wettability with the substrates should be ensured. Secondly, the ability of reliving the component segregation [108], forming amorphous phases [76], and contributing to a fine even nanometer microstructure [3,94], should be concerned to improve the mechanical properties. Besides, high laser absorption and proper dilution rate should be considered to maintain an available layer. There is no doubt that the material systems used for laser cladding on magnesium alloys are becoming increasingly complicated and diverse, and a proper design has the potential of lowering the consumption in time and economy and making the cladding process more feasible.

4.3.2. Evolution of the cladding process

4.3.2.1. New types of device. Some devices have been invented to effectively overcome the thorny problems of laser cladding on magnesium alloys effectively. Wang et al. [47] adopted a new technique to avoid the renovation magnesium parts being oxidized and/or evaporated. As shown in Fig. 17, a lot of well-arranged small holes with a diameter of about 0.3 mm distributed uniformly on the outer chamber (A) and inner chamber (B) around the outlet and inlet of the laser beam, respectively. The floating route of the shielding gas before laser irradiating was: coming from the inlet of the inner chamber, dispersing in the inner chamber, then going out of the inner chamber from the holes of top side B, and finally streaming out at the bottom side A of the apparatus. Thus, the atmosphere around the laser beam was ejected by the gas coming from the well-arranged holes before laser beam irradiated on the substrate, and the laser melting process was carried out under the circumstance of nearly pure shielding gas.

Cui et al. [109] immersed the AZ31B magnesium alloy sheet in a steel container with liquid nitrogen (−196 °C). As shown in Fig. 18, about a 2 mm deep cryogenic liquid layer over the target was used to realize rapid cooling rates and avoid surface oxidization. Compared with the plate melted with the same parameters by laser and with

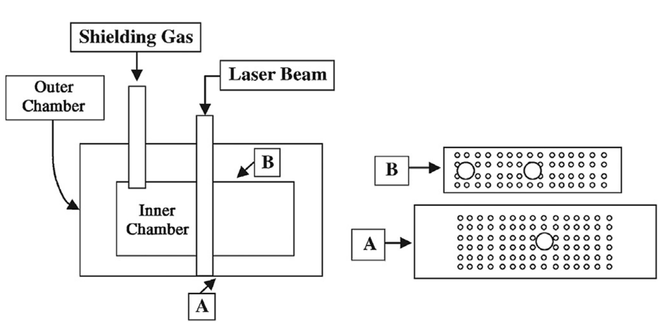

Fig. 17. Schematic diagram of the shielding gas apparatus [47].

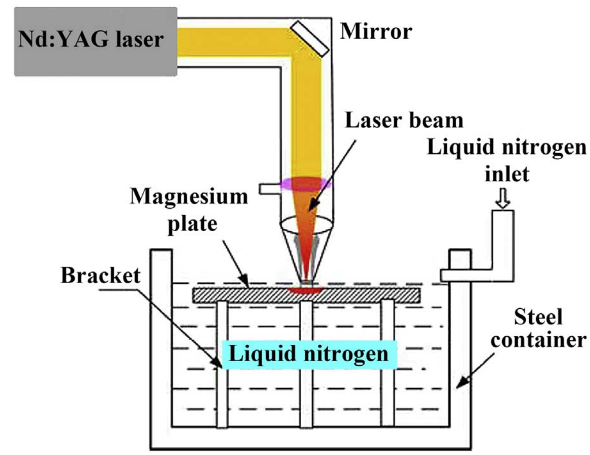

Fig. 18. Schematic diagram of LSM in liquid nitrogen [109].

99.99% high purity Ar gas (gas flow of 5 L min^{-1}) protection, the melted depth was relatively shallow and the microhardness and wear resistance was apparently improved. Results showed that the cladding coating melted in the liquid nitrogen contained a lot of worm-like nanocrystals and local amorphous structures. Obviously, the liquid nitrogen ensured the increase of cooling rate, having a better effect on the improvement of hardness and corrosion resistance on AZ31B magnesium alloy.

In addition, WC10Co2Ni cermet powders were cladded on austenitic stainless steel using the microwave hybrid heating set-up [110]. Coatings with crack-free interface and high hardness were obtained, which showed the process had the potential to be a new surface engineering technique and provided a viable option for developing the laser cladding process.

The application of newly designed equipment or treatment methods is expected to make the laser cladding process simple and efficient, and then coatings showing excellent properties would be fabricated. It is especially important to laser cladding on magnesium alloys.

4.3.2.2. Laser cladding process combined with other methods. Concerned with the unique advantages and some disadvantages of laser cladding, some researchers combined the technique with other surface treatment methods, reaching the complementary advantages. For example, a new technique called laser plasma hybrid spraying (LPHP) was studied, the special device ensured the almost simultaneous conducting of matter deposition and laser treatment. The un-fused particles after plasma spraying could be fully melted under the subsequent actions of high-energy laser, which contributed to the metallurgical bonding between the coatings and substrates, and a dense and uniformed coating could be obtained [111–113]. Yang et al. [114] realized a significant increase in the high temperature corrosion resistance of Zr-1Nb cladding tubes using the MAO + laser treatment technique. The laser melting led to the reduction in surface roughness and an increase in the compactness of the pre-oxide film. The transformation of m-ZrO_2 phase to t-ZrO_2 phase not only could improve the corrosion resistance but also had a toughening effect on the coating.

Owing to the peculiar shortcomings on magnesium alloys, the laser cladding process still has some issues to be overcome. In this case, the pretreatments or combination with other treatments become very essential. What's more, a perfect coating can be obtained and the defects which are appeared in the pretreatments can be eliminated after laser cladding process.

4.3.2.3. The biomimetic scanning strategy. Some previous studies [31,115] have developed the biomimetic scanning strategy during laser treatments. Compared with the conventional treatments, surface of the sample is partially treated instead of the whole, and the process

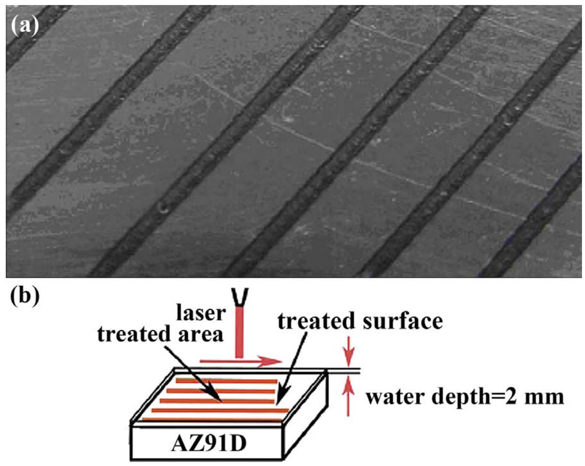

Fig. 19. (a) The treated sample surface, (b) The schematic of the selective laser treatment in the deionized water [116].

shows high efficiency and low consumption of energy. The selectively treated sample surface is similar to the naturally developed surface morphologies of particular creatures like shell, which is the reason why the method is called biomimetic scanning strategy.

Lin et al. [116] obtained an alternately hard-soft shell surface structure (Fig. 19(a)) on AZ91D magnesium alloy by selective laser cladding with Al powder, and the samples were immersed into the deionized water (Fig. 19(b)) at room temperature to obtain higher cooling rates. Because of the fine grain size and greatly uniform β-$Mg_{17}Al_{12}$ dendrites, the hardness, wear resistance, ultimate tensile strength (UTS), yield strength (YS), and elongation (EL) of the samples at room temperature were improved. Besides, this study demonstrated that larger laser powers contributed to the homogeneous microstructure and lower scanning velocities increased the amount of β-$Mg_{17}Al_{12}$. In this regard, optimization of parameters was very important.

As discussed above, the novel laser cladding methods obtained coatings with excellent microstructure and mechanical properties. The relevant investigations could provide useful information for the selective laser treatment on magnesium alloys, and then were beneficial to extend their application ranges. While, some inherent shortcomings of cladding coatings, such as the low ductility, have not been drastically solved and further studies should be carried out [116].

4.3.3. Functional gradient coating

Laser cladding of functionally graded coating is a promising method to producing high bonding strength coatings, relieving the stress concentrations and increasing the corrosion and wear resistance to prolong the lifetime of components, especially for the surface modification of large surfaces [117–119].

Yue and Li [120] studied the laser cladding process of Ni/Cu/Al functionally graded coating on magnesium substrate, and obtained a high integrity protection coating composed of (Mg), $Al_{12}Mg_{17}$, T, λ_2, λ_1, γ_1, (CuNi), (Ni) phases (Fig. 20). Because Cu had a low dilution tendency and the Ni-Cu binary phase diagram belonged to an isomorphous system, a single phase structure of (Ni) solid solution was achieved in the upper layer, which significantly improved the corrosion and wear resistance of the coating.

The biggest advantage of the functional gradient coating is that the microstructure of the coating changes gradiently, minishing the inner stress caused by the great difference between the coating and substrate, and reducing the coating crack sensitivity. Thus, the functionally graded coating realizes the compact bonding between substrate and the cladding materials which have excellent mechanical properties but cannot bond with the substrate perfectly. However, the compatibilities among different layers of the cladding materials need to be considered in the design of gradient coating.

4.3.4. HPDL cladding

The high power diode laser (HPDL) has advantages, such as better compactness, higher energy efficiency, lower running costs and more constant treatment temperature [107,121]. The material behaviors of the HPDL treatment process have been found to be different from the other traditional high power lasers (e.g. CO_2, Nd: YAG and excimer lasers):

a. Fewer cracks and less spallation for surface glazing/sealing.
b. More uniform melting/heating zones.
c. Smoother surface.
d. Better beam absorption for metallic materials.
e. More consistent and repeatable [122].

The HPDL treatments have been performed on the steel [123,124] and aluminum [125] to improve their corrosion and wear resistance. Lawrence et al. [126] demonstrated that the wetting characteristics of the ordinary Portland cement (OPC) were altered when the HPDL was used to facilitate the firing of a vitreous enamel onto the OPC surface. The reasons were that the OPC surface became smoother and more O_2 were contained after the HPDL treatment. Moreover, the findings of the work showed that the use of HPDL radiation could alter the wetting characteristics of many other materials, which was beneficial to the surface treatment on magnesium alloys. Taltavull et al. [107] used HPDL to melt the surface of the AZ91D magnesium alloy. Under optimal laser-beam power and scanning velocity, the coating was composed of a fine α-Mg matrix and β-$Mg_{17}Al_{12}$ and the corrosion resistance was improved. Therefore, it became a tendency to use HPDL into laser processing of materials. Especially, the HPDL could be used for the selective laser surface melting (SLSM) treatments, and results showed that the fracture toughness of the AZ91D magnesium alloy was improved after SLSM technique with HPDL [127,128].

4.3.5. Rapid prototyping (three dimensional laser cladding)

During laser cladding, not only the powders on the substrate surface but also a thin layer of the substrate are melted. The fabricated coating has many advantages, such as the metallurgical interfacial zone, uniform and dense microstructure, adjustable coating composition, and so on [129]. In addition, the preliminary designed three-dimensional components can be obtained through a way of layer-by-layer laser cladding. Fabricating metallic components directly by laser cladding is a new tendency in the field of manufacturing, such as the technique of rapid prototyping (RP) [130], which is also named of three dimensional laser cladding (3D LC) [131], additive manufacturing (AM) [132], laser direct metal deposition(LDMD) [133], selected laser melting [134] and so on. Nowadays, experts are changing the research focus from theory and basis application to the field of engineering application.

At the initial stage, Ni-Al and Ti-Al intermetallics were found propitious to the improvement of wear resistance of the laser cladding coatings [135]. And then a successful 3D LC of Ni85Al15 powder was carried out by Kotoban et al. [131]. A high Yb:YAG laser and a 2-channel powder feeding system were used to meet the needs of the experiment. Under the optimized processing parameters, the resulting 3D cube object with good metallographic characteristics and interface bonding was acquired, as shown in Fig. 21. With the increasing demands of magnesium alloys and the rapid evolution of laser processing equipment, deeper researches on the three dimensional manufacturing of magnesium alloys will be carried out in the future.

Obviously, the later fine machining should be considered to overcome the defects of high surface roughness in certain occasions [136]. However, high surface roughness of a biomedical implant by selective laser melting is favorable to the attachment and growth of the ambient tissues [137]. The 3D LC will lead to an evolution in the areas of parts manufacturing and greatly facilitate human life when the technique gets further developments in the future.

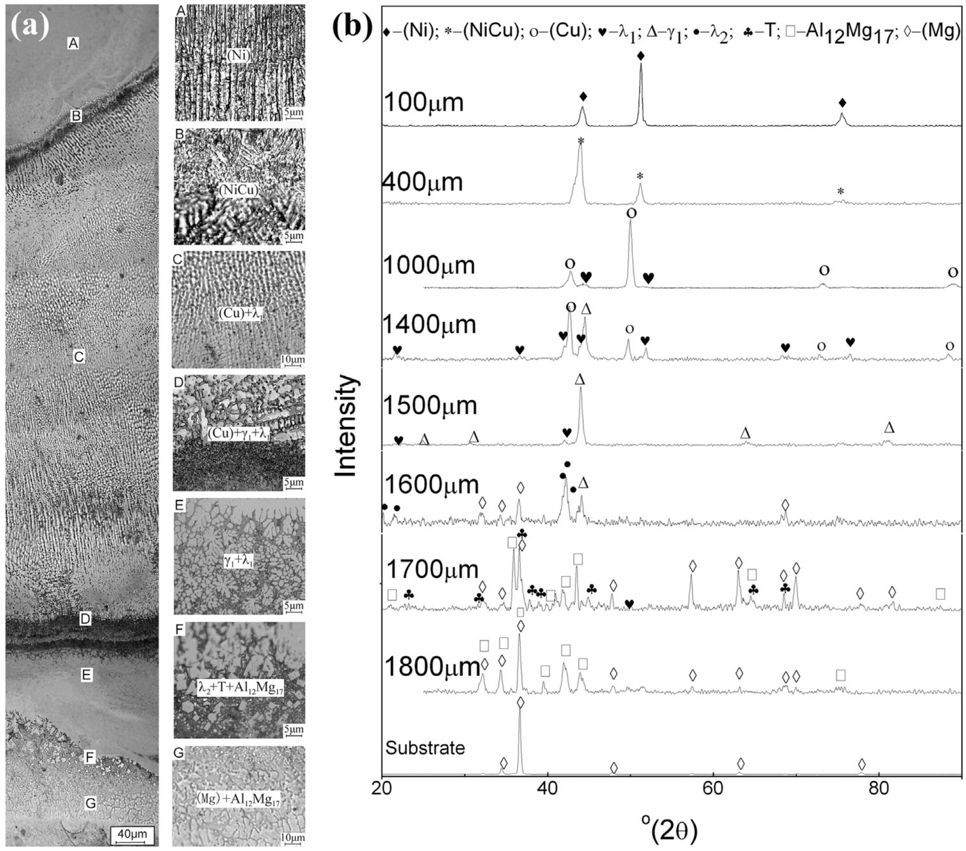

Fig. 20. (a) Microstructure of the graded coating, (b) XRD patterns of the graded coating at different section depths [120].

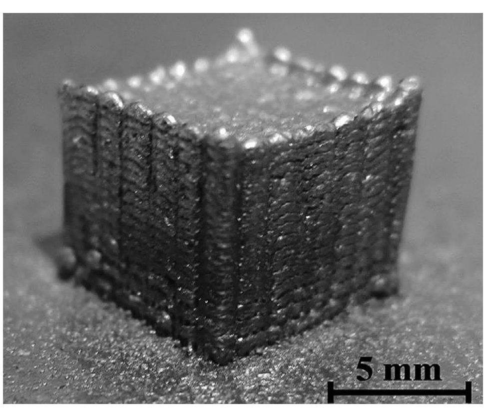

Fig. 21. Photograph of a 3D object with measured dimensions $7.4 \times 7.4 \times 5$ mm^3 obtained by 3D laser cladding of Ni85Al15 powder [131].

5. Conclusions

Magnesium alloys play an important role in the field of engineering. In recent decades, laser cladding of magnesium alloys has been a research hot spot. Though some progresses have been made, there still exist several issues to be concerned. In order to obtain coatings exhibiting metallurgical bonding with substrate, showing uniform fine microstructure and satisfactory properties, more studies should be carried out based on the issues below:

(1) Strict gas protection device or vacuum atmosphere is needed to prevent the magnesium alloys being oxidized or burnt.
(2) Some effective measures should be taken to increase the laser absorption rate, such as adopting the laser with shorter wavelength, preheating the substrate before laser cladding, adding activators on the surface of the substrate, and so on.
(3) Factors affecting the wettability between cladding materials and magnesium alloys are extremely needed. Further discussion of the mechanism of processing parameters is required.
(4) More material systems need to be developed and more mechanical properties should be concerned in order to cater to the urgent demand for magnesium alloys in the future.

Acknowledgements

This work was financially supported by the Department of Science and Technology of Shandong Province (Grant No. 2010GGX10403), PR China.

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