Growth Morphology of CuMg$_2$ in Laser Forming of AlCoCrCuFeNi Coating on Mg

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Abstract—**The AlCoCrCuFeNi high-entropy alloy coating was fabricated on pure magnesium by means of laser cladding using a direct blown powder method. The formed coating is composed of two different layers, i.e., a lower composite layer consisting of some partially melted HEA particles in a mixture of Mg and a top HEA coating. Also, some Cu was rejected into the substrate melt during the processing, resulting in the formation of CuMg$_2$ dendrites. Moreover, the dendritic structure of the CuMg$_2$ phase, which shows a faceted interface at low growth rates, is shown to undergo a transition from a faceted to non-faceted interface at relatively higher growth velocities. The change in solidification behavior of the formed CuMg$_2$ phase is likely to be due to the undercooling increase resulting from the solidification velocity increasing.**

Keywords- high-entropy alloy; laser cladding; coatings

I. INTRODUCTION

Conventional metallic alloys are typically based on the use of one or two principal elements as the matrix. Other elements may be added into these traditional alloys to improve their properties, while often results in the obvious component segregation and the formation of multiple brittle intermetallic compounds during the solidification process [1].

Since the concept of high-entropy alloys (HEAs) was proposed, the situation has been changed. Generally, HEAs are defined as alloys that consisting of between five and thirteen main elements. Due to high mixing entropy, sluggish diffusion, increased lattice strain, and cocktail effect, HEAs may give rise to a lot of promising properties. It is thus clear that HEAs open vast, unexplored combinations of alloy contents and have great potential and unique advantages to be used in many applications. Accordingly, HEAs have been received considerable attention within materials community since the HEA concept birth. Recently, various aspects of HEAs have been extensively reviewed in the literature [2].

In recent years, the HEAs also have been used to improve the properties of Mg and its alloys. For instance, the AlCoCrCuFeNi HEA has been adopted for improving the surface properties of Mg and AZ91D substrates by means of a laser cladding technique [3-7]. Nevertheless, despite the improvement of the properties of the formed AlCoCrCuFeNi HEA coatings, the results also show that the interaction between the used HEA and the substrate may occur during processing. Further improvements in laser surface forming of AlCoCrCuFeNi HEA coatings on pure magnesium and Mg-based alloys require a better understanding of the full effects related to the solidification microstructure evolution, which

are important in controlling the properties of the formed coatings. In order to smear out an influence of alloying elements from the substrate, in the present work, the AlCoCrCuFeNi HEA coatings was fabricated by using a laser cladding method on pure magnesium to evaluate the solidification behavior of the formed CuMg$_2$ phase.

II. EXPERIMENTAL PROCEDURE

The substrate materials employed in the present work were wire cut from commercially available pure Mg (purity 99.9 wt%). After that, the surface of the substrate was slightly ground with SiC emery paper to grind off the oxide layer, obtain a relatively smooth surface finish and enhance the energy adsorption from the laser beam. To eliminate the surface contaminants, the polished surface was washed with alcohol and acetone, then air dried and the laser surface treatment commenced shortly after preparation. The gas-atomized AlCoCrCuFeNi HEA particles, having composition of 16.29 Al, 17.07 Co, 16.93 Cr, 16.34 Cu, 17.11 Fe and 16.26 Ni (in at.%), were used as the initial powders.

In an argon atmosphere, the HEA powders were laser cladded onto the prepared magnesium substrates. The experiments were conducted in a laser rapid forming system consisting of a 5 kW CW CO$_2$ laser (Rofin Sinar 850), a numerical control working table and a powder feeder with a lateral nozzle. The laser beam was directed onto the substrate and the HEA particles were delivered by dry argon gas into the laser beam area using a lateral powder feeder. The laser output power was 1.4 kW, the laser beam scanning velocity was 13 mm/s, the laser spot diameter was 3 mm, the particle feed rate was 5 g/min, overlapping was fixed at 33% and the shielding gas flow rate was 2.5 l/min.

The microstructure of unetched samples was examined using a JEOL JSM-6490 scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS). A Rigaku 9 kW SmartLab X-ray diffractometer system with CuKα radiation was used for the phase identification and the crystal structure determination of both the formed MMC and the start HEA particles. The radiation conditions were 45 kV (working voltage) and 200 mA (operating current). The scanning region was ranged from 20° to 90° at scanning speed 2 °/min.

III. RESULTS AND DISCUSSION

Figure 1 shows second electron image of a transverse section of the fabricated AlCoCrCuFeNi HEA coating on

Mg by means of a laser cladding method. From this figure, it is evident that the formed coatings are mainly composed of two different regions, i.e., a lower composite region consisting of some partially melted HEA particles in a matrix of Mg and a top AlCoCrCuFeNi dense HEA coating. Moreover, the overlapping region is clearly observed as denoted by the white dashed line. The XRD results (Figure 2) indicate that the formed AlCoCrCuFeNi HEA coatings on pure magnesium are mainly composed of Mg and simple solid solution with the BCC crystal structure. In addition, the $CuMg_2$ phase was also detected within the formed HEA coatings due to the occurrence of corresponding diffraction peaks of this phase. Nevertheless, the fraction of the $CuMg_2$ phase is small owing to its low diffraction intensity in the XRD registered patterns.
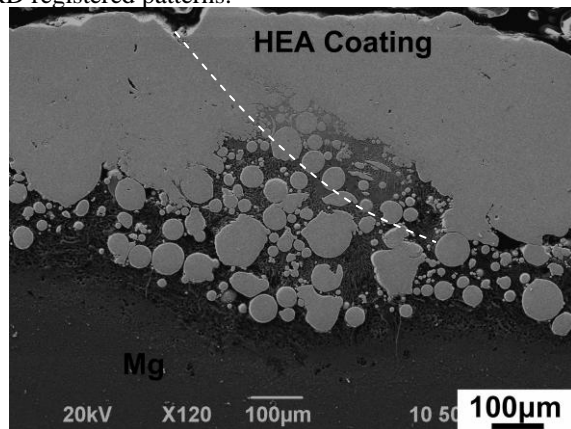

Figure 1.   The SEM image of cross-sectional microstructure of the formed AlCoCrCuFeNi HEA coating on Mg. The white dashed line is pointing to the overlapping position.
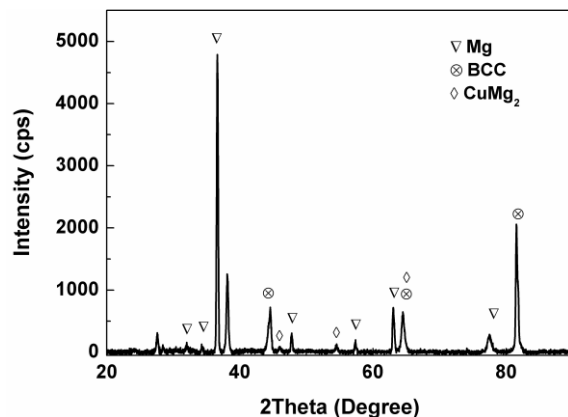

Figure 2.   Registered XRD patterns obtained for the formed AlCoCrCuFeNi HEA coatings on Mg.

Figure 3 represents the microstructure of a composite layer adjacent to the re-melted boundary between the different laser tracks at higher magnification. It can be seen that a narrow continuous planar growth layer is observed at the re-melted boundary. This is where the solidification velocity possesses the lowest value. Besides, in addition to AlCoCrCuFeNi HEA powders, in the overlapping region towards the re-melted boundary the microstructure mainly

consists of dendritic structures. The EDS-detected average composition of those dendrites between the HEA powders is given in Table 1 (in at.%). The results of the EDS analysis, together with that of the XRD analysis, help us make the conclusion that those dendrites should be composed of the $CuMg_2$ phase.

TABLE I.   EDS-DETECTED AVERANGE COMPOSITION OF DENDRITES

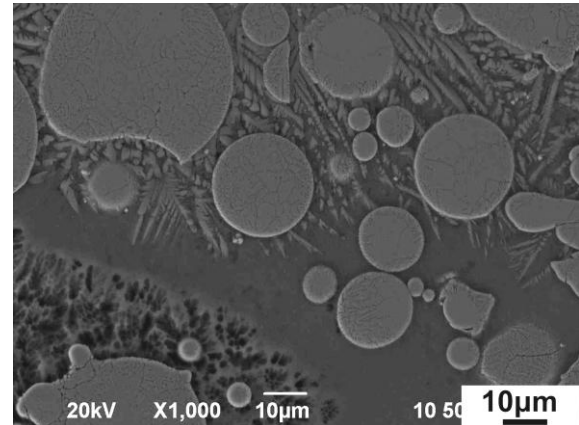| Element	Mg	Al	Co	Cr	Cu	Fe	Ni
Content	74.98	0.12	0.76	0.52	18.32	0.49	4.81

Figure 3.   The SEM image showing the microstructure adjacent to the re-melted boundary within the composite layer of the formed coating at higher magnification.

The formation of the $CuMg_2$ phase can be explained in terms of the effect of Cu rejection during the processing. In multi-component alloys, the mixing enthalpy of the binary liquid plays a crucial role in the elements segregation associated with solidification [8]. The values of liquid mixing enthalpy between Mg and HEA elements can be available from Ref. [9]. It is found that the copper has a low tendency to be attracted by (Fe, Cr, Co, Ni) due to the relatively high mixing enthalpy between Cu and these elements. On the other hand, the considerably high mixing entropy between the (Fe, Cr, Co) and Mg indicates that they also has a low tendency to mix with the substrate melt. As a result, these elements were enriched around the unmelted HEA powders during the solidification. Although the mixing enthalpy between Al-Mg and Ni-Mg is negative, they have larger negative mixing enthalpy between them and other HEA elements. This indicates that Al and Ni also tend to stay in the vicinity close to the unmelted HEA powders. Thus, only Cu could be rejected to the substrate melt during the processing. And as a result, the $CuMg_2$ dendrites within the composite layer were obtained. Besides, Figure 3 also depicts that the growth direction of some $CuMg_2$ dendrites is found to be towards the substrate. The formation of steering $CuMg_2$ dendrites could be explained in terms of the change direction of the temperature gradient, which resulted from contacting the substrate during solidification [10].
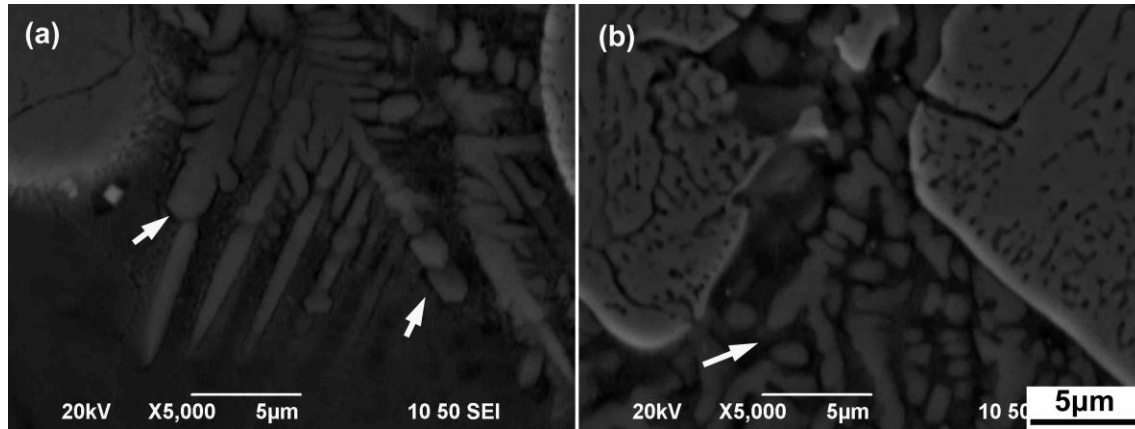
Figure 4. SEM images showing the morphogolies of the formed CuMg$_2$ phase at different locations: (a) adjacent to the re-melted boundary and (b) away from the re-melted boundary.

Moreover, the different growth morphologies of the formed CuMg$_2$ dendrites are also found within the composite layer (Figures 4). At location adjacent to the re-melted boundary, the CuMg$_2$ phase grew in a faceted manner as denoted by the arrows in Figure 4a. On the contrary, that away from the re-melted boundary the CuMg$_2$ dendrites developed in a non-faceted manner (denoted by the arrow in Figure 4b). Obviously, the change in solidification behavior of the CuMg$_2$ phase had occurred during the processing. It is well known that during the solidification of alloys, two distinctly different growth behaviors can be obtained, depending on whether the solid/liquid interface is faceted or non-faceted [11]. According to Jackson [11], it is inferred that the structure factor of the solid/liquid interface should be larger than 2 for the CuMg$_2$ dendrite shown in Figure 4a and that for the CuMg$_2$ dendrite shown in Figure 4b should be less than 2.

It is known that, during normal laser cladding, the interface morphology can normally change from planar to cell, and then to dendritic with solidification increasing. Nevertheless, it is of interesting to note that, during laser cladding, the solidification velocity increases continuously from the bottom of the molten pool to the top. So, away from the re-melted boundary, the solidification of the molten pool increases gradually. Taking into account the dependence of the driving force on faceted or non-faceted growth, Cahn [12] proposed a detailed theoretical analysis. He showed that below a certain critical undercooling the driving force is not sufficient to move the interface normal to itself, so that a faceted interface will result, characterizing by the creation and motion of steps on the interface. Later, Cahn and co-authors [13] proposed that a faceted-to-non-faceted transition will always occur at some undercooling. Since the CuMg$_2$ dendrites are located within the composite layer, during the solidification, the undercooling at the dendrite front is given by [14]

$$\Delta T = (VC_0/A). \qquad (1)$$

where V is the solidification velocity, C_0 is the given composition and A is the constant. According to Equation (1), the undercooling increases with the solidification velocity increasing. This can be used to explain the change in solidification behavior of the CuMg$_2$ dendrites. As mentioned above, due to the small distance between the re-melted boundary and the faceted CuMg$_2$ dendrites, the growth velocity of this phase should be smaller than that of the non-faceted CuMg$_2$ dendrites. As a result, the corresponding undercooling for solidification of the faceted CuMg$_2$ dendrites should be smaller than that of the non-faceted CuMg$_2$ dendrites. This means that the change in solidification behavior of the CuMg$_2$ phase is likely to be due to the undercooling increase resulting from the solidification velocity increasing.

IV. CONCLUSION

Laser surface forming of AlCoCrCuFeNi HEA coatings had been carried out on pure magnesium using a direct blown powder method. The fabricated coatings consist of the lower layer containing some partially melted HEA particles in a mixture of Mg and a top layer of the AlCoCrCuFeNi dense HEA coating. During the processing, some Cu was rejected into the substrate melt and as a result, the CuMg$_2$ dendrites were formed within the lower layer of the coatings. Also, some CuMg$_2$ dendrites adjacent to the re-melted boundary grow towards the substrate due to the change in temperature gradient resulting from contacting with the substrate. What is interesting is that the formed CuMg$_2$ dendritic structure in this system, which shows a faceted interface at low growth rates, is shown to undergo a transition from a faceted to non-faceted interface at higher velocities perhaps due to the undercooling increase resulting from the solidification velocity increasing.

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