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Mechanism of surface modification of CeO_2 in laser remelted alloy spray coatings

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Abstract

The microstructures and properties of laser remelted alloy spray coatings were studied by means of wear testing, corrosion testing, microhardness testing, scanning electron microscopy, electron probe microanalysis and transmission electron microscopy. The results show that the wear and corrosion resistance of laser remelted alloy spray coatings is remarkably increased by the addition of CeO_2. The mechanism of surface modification of CeO_2 in the laser remelted alloy spray coatings is discussed. It is suggested that the rare earth can refine the microstructure, strengthen and purify the grain boundary, and improve the morphology and distribution of eutectics and compounds.

Keywords: Tribology; Rare earth; Laser surface modification

1. Introduction

Laser remelting of thermal sprayed alloy coatings can improve their compactness, substrate bond strength, and wear and corrosion resistance [1–6]. The favorable role of rare earth elements in steels and their application in chemical heat treatment of steels have been reported [7–11]. However, publications concerning the application of rare earth elements in spray or laser modification technologies are still lacking [11–13]. Recently, Wang et al. successfully applied a rare earth (CeO_2) to modify the surface properties of the thermal spray coatings, thermal spray welding coatings and the laser-alloyed coatings, and studied the influence of rare earth elements on the microstructure, wear and corrosion resistance of the modified layers. Their research results had shown that the addition of CeO_2 can improve the morphology and distribution of eutectics and compounds, increase the hardness, and improve the wear and corrosion resistance of laser-remelted alloy coating remarkably. For example, the wear resistance of these coatings was increased by 14 times due to the addition of the rare earth element [12]. The authors suggested that the rare earth might have a refinement effect, which strengthens the grain boundaries, and improves the uniformity and compactibility of the coatings [11–13]. This paper presents further results on the influence of a rare earth, specifically Ce, on the microstructure of laser-remelted alloy spray coatings, by using scanning electron microscopy, transmission electron microscopy and electron probe microanalysis, microhardness testing, wear testing and corrosion testing.

2. Experiment

The main compositions of Fe-based amorphous self-fluxing alloy powders of 150 mesh, as used in this work, are Fe, Cr, Ni, W, Mo, B, Si and C. The ranges of each element in atomic percent are (65–70)Fe, (3–5)Cr, (2–4)Ni, (2–4)W, (1–2)Mo, (10–14)B, (4–7)Si and (2–3)C. Because the atomic ratio of metal to metalloid is about 80:20, this alloy is abbreviated to $M_{80}S_{20}$ [14]. The substrate material was common low carbon steel 1020, austenitized for 1 h at 880°C, then water quenched and tempered

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at 180°C for 1 h. This heat treatment resulted in a low carbon martensitic structure with a hardness of HRC35-45.

After cleaning, shot blasting and preheating the steel to about 200°C, we sprayed a thin Ni–Al alloy layer of about 0. 1–0. 15 mm in thickness onto the specimen by means of an oxygen–acetylene torch to provide better bonding of the coating with the substrate. Then the $M_{80}S_{20}$ and $M_{80}S_{20} + CeO_2$ alloy coatings were sprayed to a thickness of about 0.6–0.8 mm. The CeO_2 was added as particles of 200 mesh, injected into the spray, and became a component of the alloy coating.

The single-pass alloying process was conducted using a $C0_2$ laser apparatus of power 5 kW. The parameters selected in this research were as follows:

Treatment	Power	Beam spot	Power density	Traverse speed
A	2.8 kW	1 mm×4 mm	7×10^4 W cm^{-2}	10 mm s^{-1}
B	2.8 kW	1 mm×4 mm	7×10^4 W cm^{-2}	20 mm s^{-1}
C	2.8 kW	1 mm×4 mm	7×10^4 W cm^{-2}	30 mm s^{-1}
D	1.8 kW	4 mm in diameter	1.43×10^4 W cm^{-2}	2.5 mm s^{-1}

The distribution of the microhardness along the depth of the laser-remelted alloy spray coatings was measured using a Vickers microhardness indenter and a load of 100 gf. The microstructure and composition of the coatings were analyzed by means of X-ray energy dispersive spectroscopy, scanning electron microscopy, transmission electron microscopy and electron microprobe analysis.

The wear tests were performed on an Amsler testing machine, using block and ring specimens. The dimensions of the block specimens were 8 mm × 8 mm × 18 mm. The counterface ring specimens were made of 52 100 bearing steel, oil quenched at 840°C and tempered at 180°C to a hardness of 60 HRC. The wear tests were carried out under the condition of 300 N load and 0.8 m/s sliding speed without lubrication and the sliding distance was 750 m. The weight loss of the block specimens was measured and converted to the wear volume and wear rate. The mean value of three measurements was taken as the experimental results.

With a potentiostat and an HDV-7 type *X–Y* recorder, the anodic polarization curves of laser alloyed coatings obtained from different corrosive solutions were compared. The solutions used were 1N $HN0_3$, 1N H_2S0_4, 1N HCI and 5% NaCl. The corrosion rate of the laser alloyed coatings tested in 1N $HN0_3$ was determined by weight loss, and the morphology was observed by means of a Hitachi S-530 type scanning electron microscope. The coated specimens were mounted with epoxy and polished by metallographic abrasive paper of mesh grade 20, then degreased with magnesium oxide, and finally rinsed thoroughly in tap water and distilled water. Here, the untreated part on the surface was masked with neoprene. When the anodic polarization curves were recorded, the specimen was used as the study electrode, a saturated calomel electrode was the reference electrode and a Pt electrode was the auxiliary electrode. The measurement was carried out at 6 mV/s. The study area of the specimens was 2 mm × 15 mm.

3. Results and discussion

3.1. Wear and corrosion resistance

In a previous work [12], Wang et al. show that the addition of CeO_2 can increase the wear resistance quite significantly. The wear resistance of a laser-remelted spray coating with CeO_2 is 2–3.5 times that of a laser-remelted spray coating without CeO_2, as shown in Fig. 1. In another previous work [13], Wang et al. indicated that the addition of the rare earth could improve the corrosion resistance of the laser remelted spray coatings. For example, Wang et al. show that the addition of the rare earth lowers the corrosion rate of the laser-remelted alloy spray coatings by about 60% and improves the corrosion surface morphology [13].

3.2. Microhardness distribution

Fig. 2 shows the distribution of microhardness in laser remelted alloy spray coatings processed at different traverse speeds. It can be seen that the microhardness is much lower for the slowest speed. The addition of CeO_2 can significantly increase the microhardness of the coatings. For a 30 mm/s traverse speed, the microhardness of the laser-remelted zone can be increased by 100% by simply adding CeO_2, showing that CeO_2 addition is more effective for increasing the hardness of coatings than through increasing laser traverse speed. So, the addition of the rare earth elements can significantly increase the microhardness of the laser remelted alloy spray coatings.

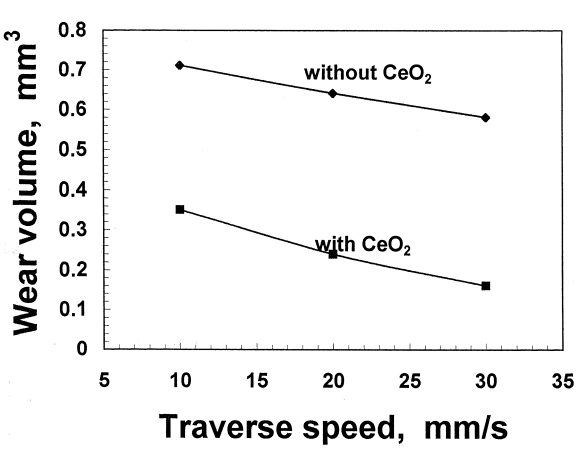

Fig. 1. Relationship between the wear volume of laser-remelted alloy spray coatings and laser traverse speed.

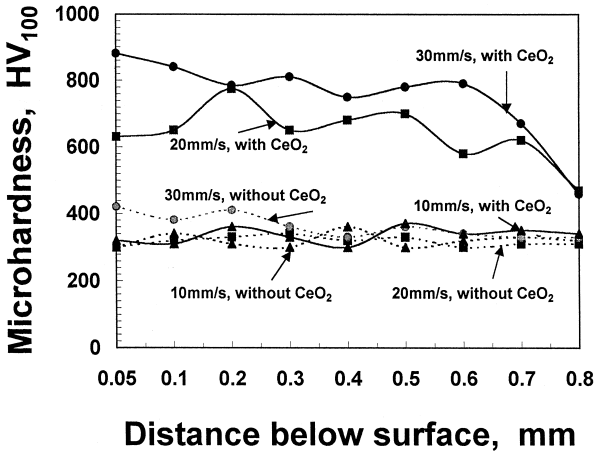

Fig. 2. Microhardness distribution in laser-remelted alloy spray coatings.

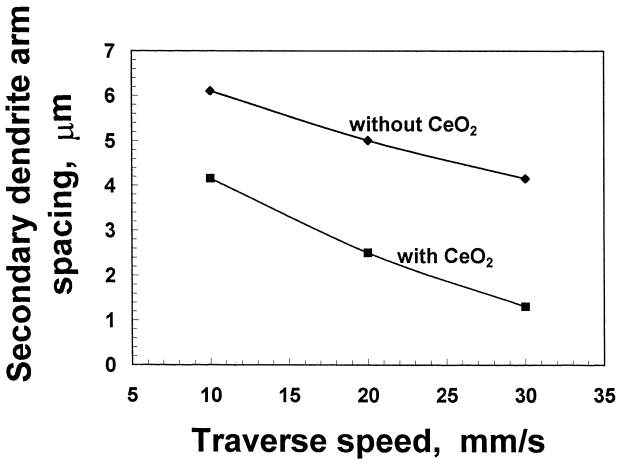

Fig. 4. Relationship between the secondary dendrite spacing in laser-remelted alloy spray coatings and laser traverse speed.

3.3. Secondary dendrite arm spacing

Fig. 3 shows the metallographic structures of the laser-remelted alloy zone. Fig. 4 shows the influence of laser traverse speed on the secondary dendrite arm spacing in laser remelted alloy spray coatings. It can be seen that, for both coatings with or without CeO_2, increasing the traverse speed shows a refinement in their microstructure and a reduction in secondary dendrite arm spacing. The addition of CeO_2 makes the refining effect more significant. It can also be seen that the addition of CeO_2 can improve the morphology and distribution of eutectics and compounds. In addition, the concentration of microvoids in the molten zone is clearly reduced by the addition of the rare earth.

3.4. Eutectics and compounds

TEM observation on the laser-remelted alloy spray coatings with CeO_2 revealed that more eutectics and compounds with regular morphology are distributed at the interdendritic boundaries, as shown in Fig. 5a. Mostly, these spherical and block compounds are boroncarbide. Some small spherical multi-phase particles gather at the interdendritic boundaries. In contrast, in the laser remelted alloy spray coatings without CeO_2, the amount of eutectics and compounds is obviously less than that in the laser remelted alloy spray coatings with CeO_2. The eutectics

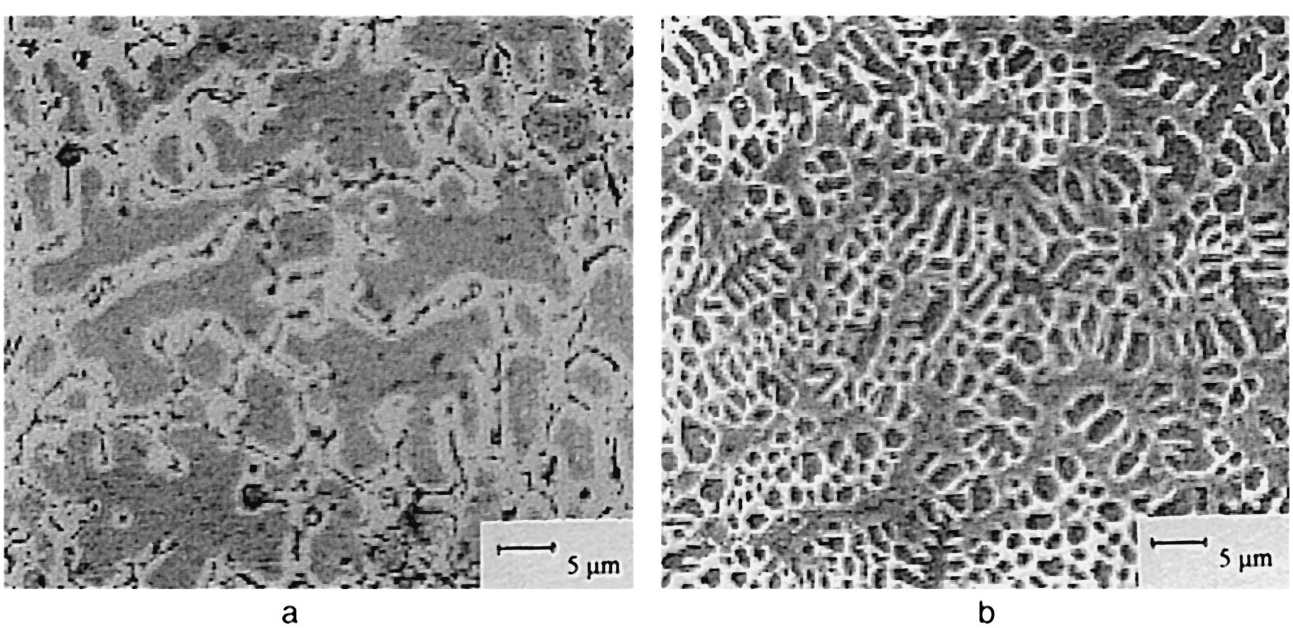

Fig. 3. Microstructures revealed by SEM of different laser-remelted alloy spray coatings. (a) Without CeO_2, 30 mm/s; (b) with CeO_2, 30 mm/s.

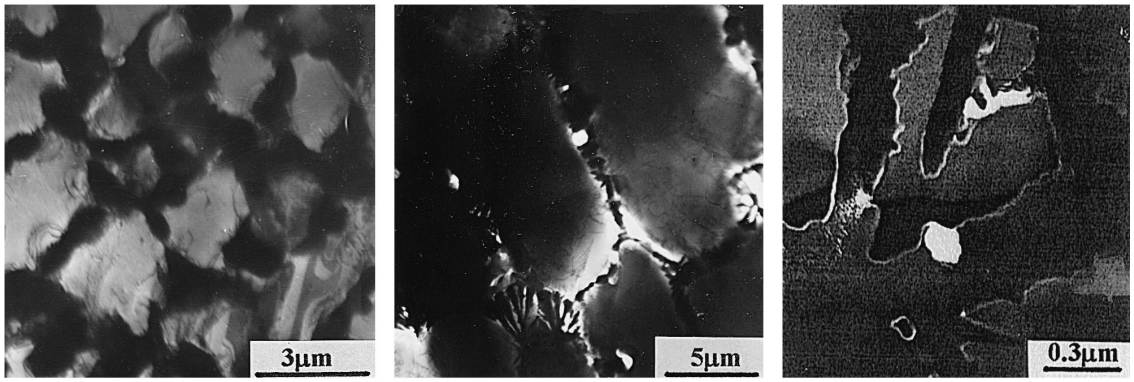

Fig. 5. Microstructures revealed by TEM of different laser-remelted alloy spray coatings. (a) With CeO_2, 2.5 mm/s; (b) without CeO_2, 2.5 mm/s; (c) without CeO_2, 2.5 mm/s.

and compounds in the coatings have different forms and sizes. Also, their distribution is not even, as shown in Fig. 5b. The microstructures of these compounds are complex. For example, they are blocked in knots, plate-like and elbow-like (FeCr) δ phase. There are needle-like M3B2 and branched $M_{23}(CB)_6$. Also, there are some randomly gathered small multiphase particles with an irregular distribution. Fig. 5c shows some branched and granular eutectic compounds in the laser remelted alloy spray coatings without CeO_2.

3.5. Martensite

TEM observation shows that the laser remelted alloy spray coatings with or without CeO_2 consists of dendrites and interdendritic eutectics. For the laser remelted alloy spray coatings with CeO_2, the dendrites are small equiaxial grains separated by wide eutectics; while for the laser remelted alloy spray coatings without CeO_2, the dendrites are usually bigger and uneven, grains separated by eutectics with different widths. Electron microanalysis on many different observation fields of many samples shows that there is no martensite in the laser remelted alloy spray coatings without CeO_2, either in the dendrite structures or in the eutectic structures. However, martensitic structure, as well as austenitic structure with lower density of dislocation, can be found in the laser remelted alloy spray coatings with CeO_2. The martensitic structure has a high density of dislocation and fine twin. The morphology of martensitic structure includes lath-like, leaf-like, blocky and chrysanthemum-like shapes. Some TEM micrographs of martensitic structure in the laser remelted alloy spray coatings with CeO_2 are shown in Fig. 6. So, the addition of the rare earth can significantly improve the microstructure, promote martensitic transformation, make grain refinement and spheroidize eutectic compounds.

4. Discussions

Generally speaking, increasing the hardness of materials can increase their wear resistance. Indeed, in this case, the addition of CeO_2 can increase the hardness of the laser remelted alloy spray coatings, as shown in Fig. 2. How-

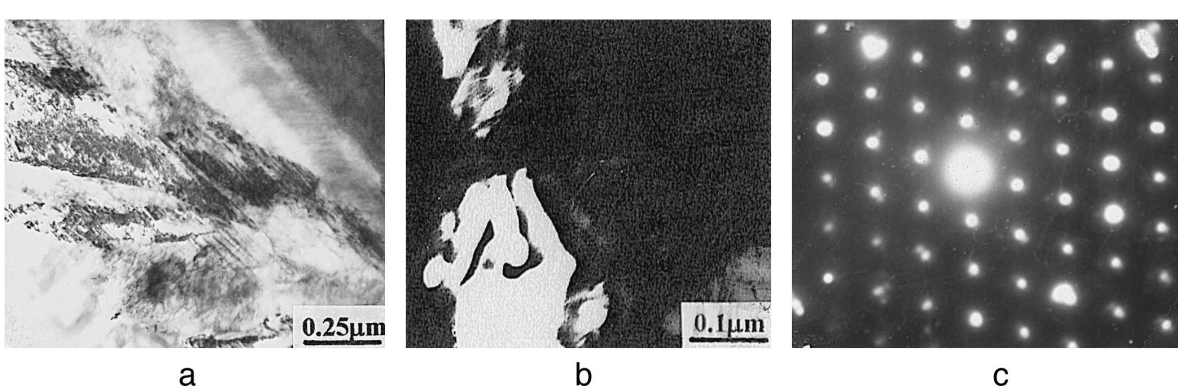

Fig. 6. Martensitic structure in laser-remelted alloy spray coatings with CeO_2. (a) Microstructure of martensite; (b) eutectic of martensite and $M_{23}(CB)_6$; (c) diffraction pattern for (b).

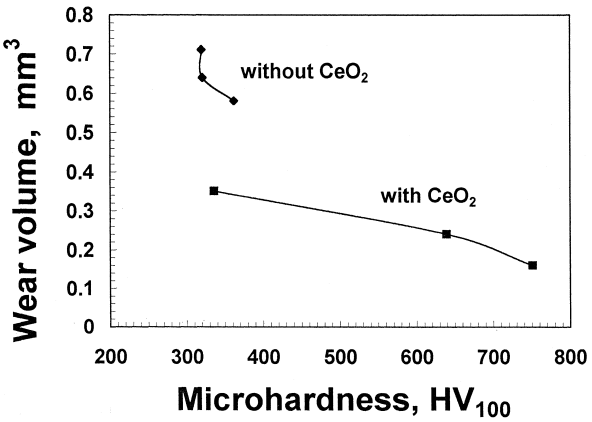

Fig. 7. Relationship between the wear volume and average microhardness in laser-remelted alloy spray coatings.

ever, in some cases, such as for a laser traverse speed of l0 mm/s, the addition of CeO_2 cannot obviously increase the hardness of the laser remelted alloy spray coatings. But it can obviously increase the wear resistance of the coatings, as shown in Figs. 1, 2 and 7.

As mentioned earlier, the addition of CeO_2 refines the microstructure of laser remelted alloy spray coatings. The addition of CeO_2 can improve the morphology and distribution of eutectics and compounds; the gross dendrite structure is replaced by fine equiaxed eutectics. The refined dentritic boundaries form a more compact network structure. As a result, the hardness of laser remelted alloy spray coatings can be increased. Fig. 8 shows the relationship between the hardness and the secondary dendrite arm spacing of the laser remelted alloy spray coatings. It can be seen that decreasing the secondary dendrite arm spacing can increase the hardness and thereby increase the wear resistance of the laser remelted alloy spray coatings. Usually, the microstructure of the laser remelted alloy spray coatings can be refined by increasing the laser traverse speed. However, when the secondary dendrite arm spacing of the laser remelted alloy spray coatings with CeO_2 is the same as that of the laser remelted alloy spray coatings

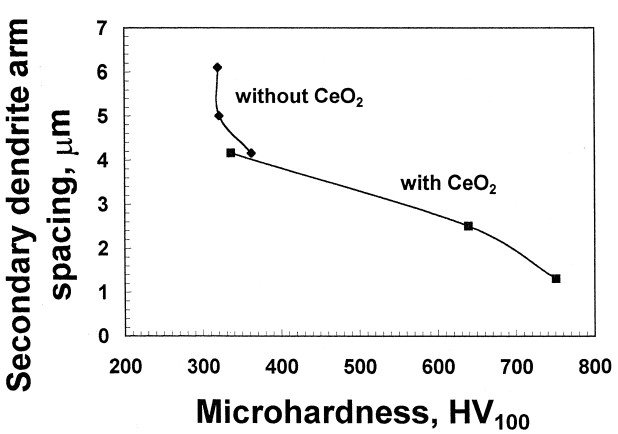

Fig. 8. Relationship between the secondary dendrite spacing and average microhardness in laser-remelted alloy spray coatings.

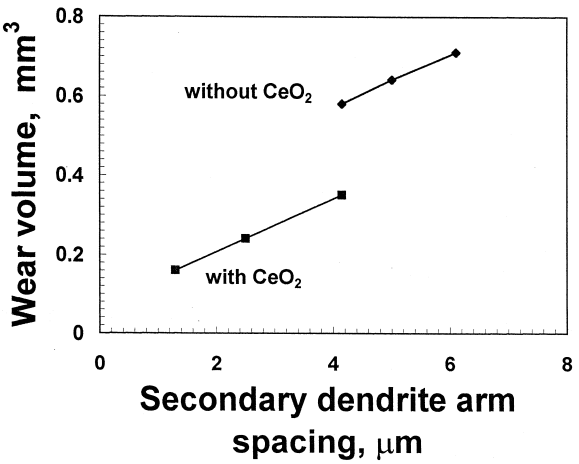

Fig. 9. Relationship between the wear volume and secondary dendrite spacing in laser-remelted alloy spray coatings.

without CeO_2, the laser remelted alloy spray coatings still exhibit a higher wear resistance, as shown in Fig. 9. In this case, the wear resistance is doubled by the addition of the rare earth. Therefore, the refining and hardening of the microstructure is not the only reason for the increases in wear resistance of the laser remelted alloy spray coatings by the addition of CeO_2.

This problem can be discussed by using the Hall–Petch equation [15]. Where, the d values are the same for the two different coatings. However, the addition of CeO_2 mainly changed σ_0, and k, in particular k is increased by the addition of CeO_2, because the constant k describes the difficulty of transmitting slip across the grain boundary and increases as a result of solute segregation at the grain boundary or ordering of the material. In other words, k expresses the strength of the grain boundary. It has been shown that grain boundaries are an active element of the microstructure and they take part in the processes occurring in the material. Particularly in the initial stage of plastic deformation, they can act as the most important points of dislocation generation and annihilation. Also, grain boundary characteristics can affect the macroscopic behavior of material during plastic deformation [16]. If different grain boundaries can be expressed by different characteristic functions of grain boundaries, the addition of CeO_2 certainly changed the characteristic function. Rare earth element segregation at grain has been identified. Rare earth oxide particles are considered to act as sources for local rare earth segregation [17]. It has been found that grain growth was hindered in the doped scales due to the rare earth addition, implying that Ce segregation and/or CeO_2 particles were pinning the boundaries. Also, it is suggested that the surfaces of dispersed rare earth oxide particles may act as sinks for impurities. Rare earth sulphides/oxysulphides are stable in the solid alloy, reducing the amount of free S [17]. The electron probe microanalysis of a laser remelted alloy spray coating with CeO_2 showed that the content of Ce in the coating is very small

—less than 5% can be detected, and it is also found that its content is higher at the grain boundaries than in the grains. Thus, those small multi-phase particles gathered at the interdendritic boundaries probably are rare earth compounds formed with some impurity elements, which strengthened and purified the grain boundaries and increased the difficulty of transmitting slip across the grain boundaries.

Therefore, the reason for the increase in wear and corrosion resistance brought about by the addition of CeO_2 is as follows:

1. The rare earth has a refinement effect, i.e., it can decrease the dendrite arm spacing remarkably;
2. The rare earth can strengthen and purify the grain boundaries and change the characteristics of grain boundaries;
3. The rare earth can spheroidize the medics and compounds, and improve their morphology and distribution;
4. The rare earth can promote martensitic transformation;
5. The rare earth can decrease the concentration of microvoids and improve the uniformity and compatibility of microstructure.

As a result, the microhardness, the wear and corrosion resistance of laser remelted alloy spray coatings can be significantly increased by addition of the rare earth.

5. Conclusions

The addition of CeO_2 refines the microstructure in laser remelted alloy spray coatings, decreases the dendrite arm spacing, strengthens and purifies the grain boundary, promotes martensitic transformation, and improves the morphology and distribution of eutectics and compounds. Therefore, the microhardness, the wear and corrosion resistance of laser remelted alloy spray coatings can be remarkably increased by the addition of the rare earth.

6. Biographies

Dr. You Wang obtained his Masters Degree and his PhD degree from Harbin Institute of Technology in 1981 and 1989 respectively. Then he completed his post-doctoral research at Tsinghua University from 1989 to 1991. He taught at Heilohgjiang Commercial University from 1977 to 1978 and at Harbin Shipbuilding Engineering Institute from 1981 to 1986. He became an Associate Professor at Tsinghua University in 1991. Then, he taught at Beijing University of Aeronautics and Astronautics from 1991 to 1994. He was promoted as a Full Professor in 1993. He worked at the University of Manitoba, Canada from 1994 to 1995 as a Visiting Scientist. From 1995 to 1997, he worked at the University of Illinois at Chicago as a Research Fellow, and at same time, worked at the US national Institute of Standards and Technology as a Guest Scientist. Now, he is a Senior Researcher at Southern Methodist University. He is a specialist in failure analysis of Chinese Mechanical Engineering Society. He was invited as a Guest Professor at Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. Up to now, he had published over 90 papers in the field of materials Science and Technology, Tribology and Surface Engineering.

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JiaJun Liu is a Professor of the Department of Mechanical Engineering, Tsingua University, China. He graduated from Tsinghua University in 1953, and obtained PhD degree from MBTY of the former Soviet Union in 1959. Since then is has been working as a group leader at the Department of Mechanical Engineering and Tribology Research Institute of Tsinghua University. His main research directions involve sliding wear mechanism of materials under lubrication, tribology of ceramic cutting tools and polymeric matrix composite materials, surface engineering, etc. Currently he is the Associate-Director of Tribology Research Institute of Tsinghua University, Associate-Director of Surface Engineering Institute CMES, Associate-Editor in Chief of Chinese Journal of Tribology and China Surface Engineering.

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