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Laser resolidification of Zn-rich Zn-Ag peritectic alloys ①

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[Abstract] Laser remelting experiments were performed by a 1.0kW continuous CO_2 laser to investigate the rapid solidification behavior of Zn-rich Zn-Ag peritectic alloys. Three kinds of microstructures occurrs with the varying of laser scanning speed and Ag content in the alloys. It is mainly plate-like single-phase cellular η when the Ag content was lower than 1.8% (mole fraction). As the Ag content increased, instead of typical structure of primary dendrites of ε surrounded by peritectic η, a two-phase plate-like η+ ε with primary dendrites of ε is found when the laser scanning speed was higher than a critical value. Intercellular spacing of cellular η or interphase spacing of two-phase couple growth η+ ε decreases with increasing laser scanning speed.

[Key words] Zn-Ag alloys; laser remelting; peritectic; couple growth
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1 INTRODUCTION

Peritectic reactions are widely encountered when a solid phase reacts with a liquid phase to produce a second solid phase during the solidification process of the liquid alloy. Peritectic solidification study has attracted an increasing attention during the last decade since most peritectic materials are of technologically importance, such as structural materials steels and copper alloys, permanent magnetic Co-Sm-Cu and Nd-Fe-B, and high temperature superconducting materials $YBa_2Cu_3O_y$[1~3]. Most of the previous investigations on peritectic reaction were on equilibrium or near equilibrium solidification process, such as nucleation, peritectic transformation, couple growth, solid segregation and phase selection[4~7]. Because of the complexity of the peritectic reaction under non-equilibrium conditions and the formation of complex microstructures, understanding of the rapid solidification behavior of peritectic alloys is still not in-depth.

The obtained microstructure of peritectic reaction depends on the solidification condition and alloy composition. The typical microstructures are such as the cellar structures of primary and peritectic phases in Sn-Cd peritectic alloys, two-phase plate-like structure in Zn-Cu alloy and couple growth of primary and peritectic phases in Ni-Al, Ti-Al, Fe-Ni and Zn-Ag peritectic systems[5~12]. Couple growth of two phases is one of the key points in Ref. [6, 8]. In general, only when the growth speed is fast enough to prevent the formation of the primary phase and get a planar solid-liquid interface, the couple growth could be found close to the peritectic reaction temperature[9, 13]. The attempts to achieve two-phase couple growth in peritectic alloys by rapid solidification, especially by laser remelting, have failed except for studies on Ni-Al, Ti-Al and Fe-Ni alloys[6, 8]. The eutectic-like lamellar structure has been found in as-spun ribbons of Zn-6.3Ag alloy. However, the laser remelting rapid solidification behavior of Zn-rich Zn-Ag alloys has never been reported. The present work investigates the effects of various laser scanning speeds and Ag contents on phase transformation behavior of the remelted zones of Zn-rich Zn-Ag peritectic alloy in order to gain more insight into the non-equilibrium formation of couple growth in peritectic systems.

2 EXPERIMENTAL

Six Zn-Ag alloys containing 0.6%, 1.8%, 3.1%, 4.4%, 6.3% and 9.0% Ag (mole fraction) respectively were prepared by melting Zn (99.99% in purity) and Ag plates in an induction furnace. The specimens with gauge of 30mm × 50mm × 8mm were cut from the middle part of the alloy ingot and ground on 1000 grit SiC paper to ensure a glazed surface for each specimen. Before laser treatment, some self-made light-absorbent was coated on the surface of the specimens to ensure the uniformity and sufficiency of laser absorbing.

The laser scanning speed varied from 16.7mm/s to 120mm/s with a scanning power of 1.0kW, a spot diameter of 1.0mm and a resulting power density of 320W/mm^2. During the laser treatment, a flow of argon was blown onto the surface in order to reduce oxidation of the molten pool.

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The specimens were polished and then etched in a 1% nitric acid solution. The sections of the specimens were studied by optical and scanning electron microscopes. Intercellular spacing of single-phase cellular η and interphase spacing of two-phase couple growth in the region near surface were measured by transmission electron microscopic.

3 RESULTS AND DISCUSSION

The Zn-rich Zn-Ag binary phase diagram is shown in Fig. 1[14], in which a peritectic reaction, $\varepsilon_{c_5} + L_{c_2} = \eta_{c_{11}}$, takes place at 431 ℃. Phase ε is termed the primary $AgZn_3$ phase and part of η (Zn-rich solid solution) the peritectic phase. c_L, c_ε, c_η refer to the compositions of liquid, primary and peritectic phases respectively.

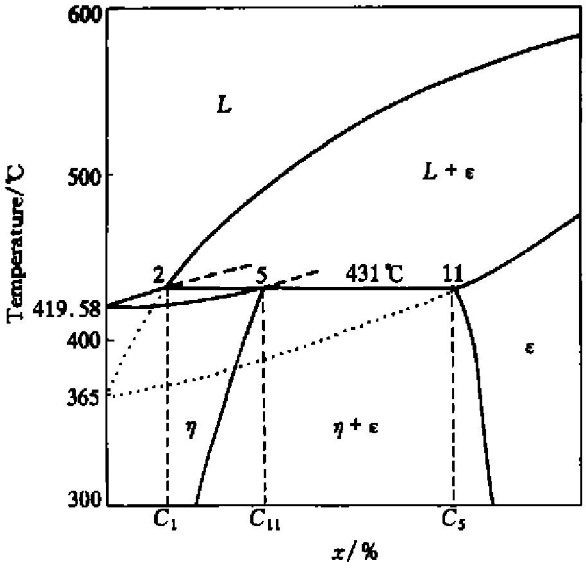

Fig. 1 Zn-Ag binary phase diagram

A single-phase plate-like cellular ε forms in Zn-0.6% Ag (mole fraction) alloy with a laser scanning speed of 16.7 mm/s, as shown in Fig. 2(a). In fact, no matter how the laser scanning velocity varied, the microstructure of Zn-0.6Ag and Zn-1.8Ag alloys is always the single-phase plate-like cellular ε. For Zn-3.1Ag and Zn-4.1Ag alloys, two phase ε+ η begin to occur and the microstructure is a two phase plate-like ε+ η with a primary ε dendrite. The volume fraction of primary ε phase decreases with increasing the laser scanning speed. A near fully two-phase plate-like ε+ η dominates with little of primary ε phase when the laser scanning speed reached 90 mm/s for Zn-3.1Ag alloy, as shown in Fig. 2(b). The laser scanning speed with fully two-phase microstructure for Zn-4.4Ag alloy is 120 mm/s. For Zn-6.3Ag and Zn-9.0Ag alloys, a structure of two phase plate-like ε + η with primary dendrites of ε is observed with different laser scanning speeds, as shown in Fig. 2(c). Fig. 3 shows the variation of microstructures with laser scanning speed and Ag content in the alloys.

Fig. 4 shows the TEM micrographs for the longitudinal sections of the laser remelting specimens. They show the formation of the single-phase plate like cellular η for much lower Ag content and two phase-like ε+ η couple growth for high Ag content respectively. Fig. 5 shows the relationship between intercellular spacing of η phase and the laser scanning

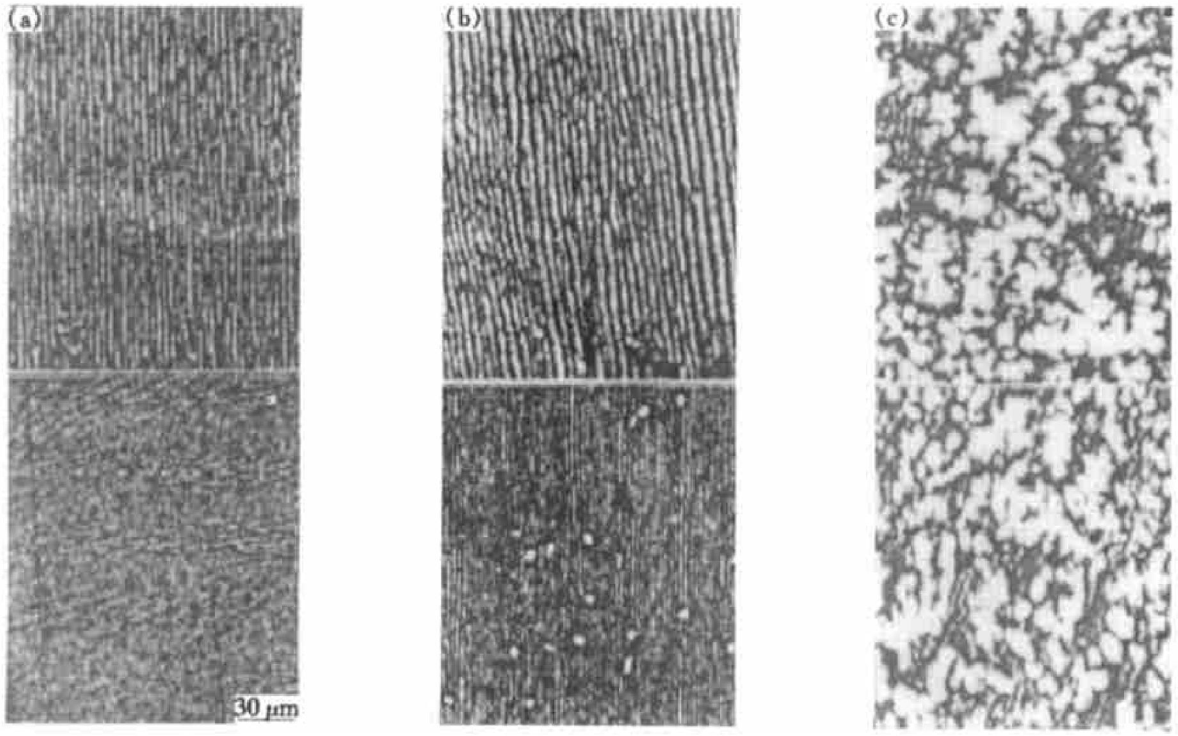

Fig. 2 Laser remelting rapid solidification microstructures for Zn-Cu alloys at different laser scanning speeds (v)

(a) —Zn-0.6Ag, v = 16.7 mm/s; (b) —Zn-3.1Ag, v = 90 mm/s; (c) —Zn-6.3Ag, v = 120 mm/s

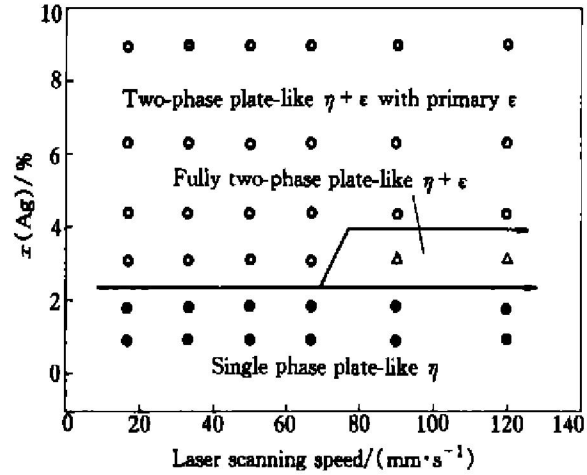

Fig. 3 Variation of microstructures with laser scanning speed and Ag content

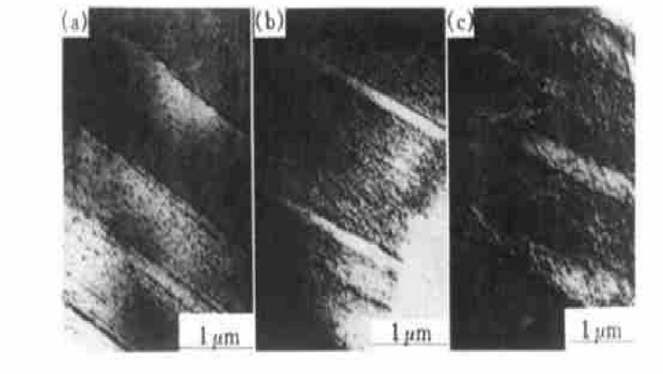

Fig. 4 TEM micrographs of vertical sections at laser scanning speed of 90 mm/s
(a) —Zr-1.8% Ag (mole fraction);
(b) —Zr-3.1% Ag (mole fraction);
(c) —Zr-4.4% Ag (mole fraction)

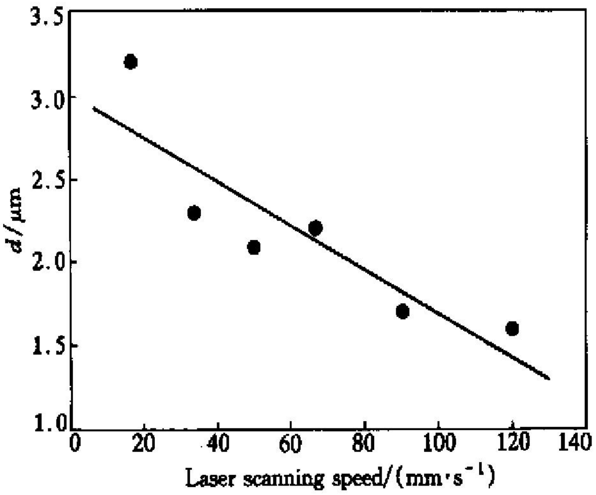

Fig. 5 Relationship between intercellular spacing (d) and laser scanning speed for Zr-0.6Ag alloy

speed for Zr-0.6Ag alloy. It could be seen that the spacing decreased rapidly with increasing laser scanning speed. The variations of interphase spacing of two-phase plate-like $\varepsilon+\eta$ with laser scanning speed for Zr-3.1Ag and Zr-6.3Ag alloys are shown in Fig. 6. The spacing decreases with increasing scanning speed. The same relationship could be found in Zr-4.4Ag and Zr-9.0Ag.

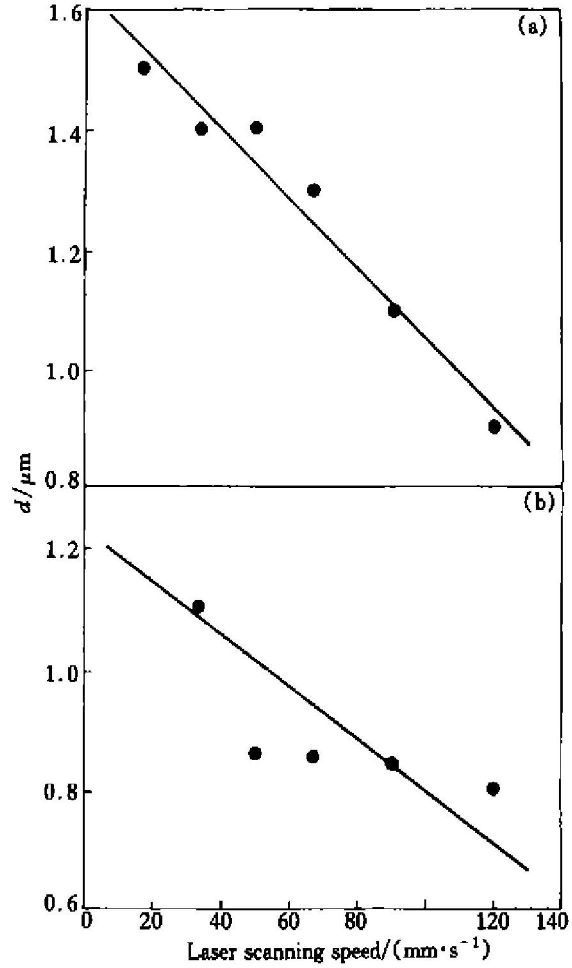

Fig. 6 Variations of interphase spacing (d) of two-phase laser scanning speed
(a) —Zr-3.1Ag; (b) —Zr-6.3Ag

Some researchers pointed out that the couple growth in Sn-Cd peritectic alloys is unstable[7]. Lee and Verhoeven[5] reported two-phase cellular couple growth of γ and γ' in Ni-Al peritectic alloys at high G/V conditions; Busse observed two-phase couple growth with an inter-phase of 30 μm in Ti-53.4% Al (mole fraction). Recently, a eutectic-like lamellar structure is reported in Fe-Ni alloy[6]. However, most of these investigations were carried out close to the limit of constitutional supercooling. Up to now, no experiments were carried out to study the couple growth in peritectic systems by laser remelting rapid solidification.

The grain growth velocity for laser remelting rapid solidification is lower than 10^2 mm/s, which is higher than the velocity for normal solidification but far lower than that for as-spun rapid solidification. For the given Zr-Ag peritectic alloys, there is a critical value of laser scanning speed, which is 90 mm/s and 120 mm/s for Zr-3.1Ag and Zr-4.4Ag respectively. Fully two-phase $\eta+\varepsilon$ could be obtained at speed above the critical value. Primary ε dendrites could also be found when the Ag content was higher than 3.1% (mole fraction). This was not reported in the other peritectic systems. In fact, for the microstructures of Zn-Ag peritectic alloys with composition between c_L and $c_ε$, the grain growth temperature varies with the growth velocity, which depends direct ratio on the laser scanning speed. When the growth velocity was near the constitutional supercooling limit, the two-phase plate-like η+ ε appeared. As the laser scanning speed increased, the growth velocity of the primary phase was improved and predominated in the phase transformation process before the η phase came into being by peritectic reaction. When the laser scanning speed increased too much, the η phase could appear directly from the liquid phase without any peritectic reaction and formed two-phase η+ ε structure. During this transformation process, the primary ε phase would compete with that of plate-like ε+ η until the later dominated. When the laser scanning speed was much higher than the critical value, the growth velocity increased to a certain degree and the single-phase ε would replace the two-phase couple growth structure.

It could be seen from Fig. 6 that the inter-phase spacing of two-phase plate-like ε+ η varies from 1.47 μm to 1.31 μm as the Ag content in the peritectic alloys increases from 3.1% to 6.3% with the laser scanning speed of 16.7 mm/s. These values of spacing are greater than those for other peritectic systems such as Al-Cu, Ti-Al and Ni-Al alloys but almost the same as that for Fe-Ni system as it was reported in Ref. [6] that the growth of two-phase turned unstable as the amount of secondary phase increased in Fe-Ni peritectic system. As studied in this paper mentioned just now, when the Ag content increased from 3.1% to 6.3%, the volume fraction of ε in the two-phase plate-like η+ ε increased from 9% to 50% and the growth of two-phase structure was always stable. This character is very different from the laser remelting rapid solidification behavior of Fe-Ni peritectic alloys system.

4 CONCLUSIONS

1) When the Ag content is lower than 1.8%, the laser remelting microstructure is still the single-phase plate-like cellular η, no matter how the laser scanning speed varies.

2) For Zn-3.1Ag and Zn-4.4Ag alloys, there is a critical value of laser scanning speed, which is 90 mm/s for the former and 120 mm/s for the later. Two phase plate-like ε+ η with a primary ε phase occurrs when the laser scanning speed is lower than the critical value, and fully two-phase plate-like couple growth η+ ε can be obtained at speed above the critical value.

3) The intercellular spacing of single-phase plate-like η and inter-phase spacing of couple growth peritectic ε+ η decreases with increasing laser scanning speed. The inter-phase spacing of couple growth is also reduced as the Ag content increases.

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