

Evolution of Divorced Eutectic Structure in NiCoCrFeAl Eutectic High Entropy Alloy by Selective Laser Melting

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Abstract: In this study, a NiCoCrFeAl eutectic high entropy alloy (EHEA) was prepared by selective laser melting (SLM). The sample was a cellular eutectic structure composed of BCC/B2 cells and FCC cell boundaries. The results show that under the extremely high-temperature gradient and cooling rate of selective laser melting, the microstructure characteristics of cellular eutectic produced by strong non-equilibrium solidification will be greatly affected by scanning speed and laser power. The reasons for the formation of the cellular structure are as follows: The growth rate of B2 dendrites is much faster than that of eutectic at high undercooling, resulting in hypoeutectic structure, which evolves into divorced eutectic under certain conditions. When the laser scanning speed is high, the cooling rate of the molten pool is increased, and the primary arm spacing of dendrites is shortened; thus, the cell structure size is refined. However, at a lower scanning speed, the cyclic thermal loading time of the deposited materials is prolonged, which is beneficial to the diffusion and enrichment of elements and promotes the amplitude modulation decomposition process of the BCC phase in the cell. These results provide new insight into the formation and evolution behavior of the rapidly solidified structure of SLMed EHEAs.

Keywords: additive manufacturing, high entropy alloy, cellular structure, rapid solidification

1 Introduction

Eutectic high entropy alloy (EHEA) is a multi-element alloy proposed by Lu et al.[1] in 2014, which combines the advantages of eutectic alloy and high entropy alloy. It usually has a microstructure of hard BCC phase and soft FCC phase, which can achieve a good combination of strength and plasticity. As a eutectic alloy, EHEAs have a narrow crystallization temperature range and good fluidity and are suitable for various preparation processes such as casting, powder metallurgy, and additive manufacturing.

During the rapid solidification of SLMed NiCoCrFeAl EHEAs, in addition to the formation of the conventional lamellar eutectic structure, a cellular structure resulting from non-equilibrium solidification also occurs[2-4]. At present, there is no unified explanation for why the cellular eutectic structure different from the traditional lamellar structure is formed in SLMed NiCoCrFeAl EHEAs, and this cellular structure is very similar to the

divorced eutectic that the traditional binary eutectic alloy evolved from hypoeutectic during rapid solidification[5]. Therefore, in this study, Ni_{32.5}Co₁₅Cr₁₀Fe₂₃Al_{17.5}Mo_{1.5}W_{0.5} eutectic high entropy alloy was designed based on Thermo-Calc thermodynamic software and prepared by SLM. The formation mechanism and evolution behavior of the cellular structure of SLMed EHEAs were systematically studied by adjusting SLM process parameters.

2 Experimental procedure

Ni₃₅Fe₃₆Cr₁₀Al₁₇Mo₂ and Ni₃₀Co₃₀Cr₁₀Fe₁₀Al₁₈Mo₁W₁ pre-alloyed powders with particle size distribution ranging from 15 to 53 μm prepared by gas atomization were mixed for 12 hours according to the mass ratio of 1:1, to achieve a nominal Ni_{32.5}Co₁₅Cr₁₀Fe₂₃Al_{17.5}Mo_{1.5}W_{0.5} composition. All parts are manufactured by BLT-S200 SLM machine and protected by argon. The experimental parameters used in this work are as follows: the laser beam diameter is 80 μm, the layer thickness (40 μm) and the hatch spacing (50 μm) are unchanged, and the laser power (190-330 W) and scanning speed (600-1200 mm/s) are changed at the same time. Adjacent layers are rotated by 67°. The microstructure and chemical composition were characterized by a field emission scanning electron microscope (SEM, TESCAN MIRA3) and transmission electron microscope (TEM, FEI Talos F200X) equipped with an energy dispersive spectrometer (EDS).

3 Result and discussion

Fig. 1(a1-a3) show the cellular structure morphology perpendicular to the building direction at different laser scanning speeds. With the increase in scanning speed, the cellular structure size becomes smaller. The statistical results in Fig. 1(b) show that with the increase of the volume energy density (VED) from 49.5 J/mm³ to 145.8 J/mm³, the wall thickness of the FCC phase increases from ~100 nm to over 180 nm, while the volume fraction of BCC phase decreases from ~63% to ~48%. Fig. 1(c) shows the average diameter of cellular eutectic decreases from 615.3±53.7 nm at 600 mm/s to 487.4±19.0 nm at 1200 mm/s, which is because the cooling rate of the molten pool increases with the increase of scanning speed, and the growth rate of dendrites accelerates, thus reducing the primary arm spacing of dendrites. The results show that under the extremely high-temperature gradient and cooling rate of selective laser melting, the microstructure characteristics of cellular eutectic produced by strong

non-equilibrium solidification will be greatly affected by the scanning speed and laser power.

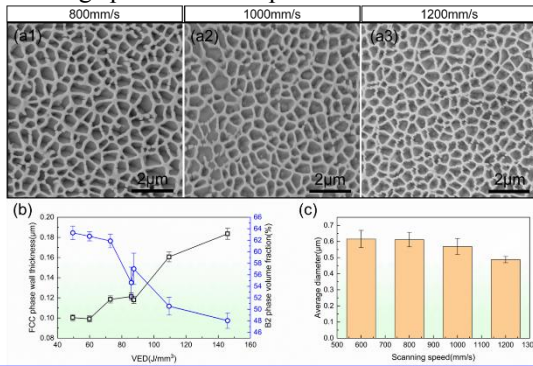


Fig. 1(a1-a3) show the morphology of cellular eutectic at scanning speeds of 800 mm/s, 1000 mm/s and 1200 mm/s; (b) The variation of FCC phase thickness and B2 phase volume fraction with VED; (c) The change of the average diameter of the cellular eutectic with the scanning speed.

According to the HADDF images at different scanning speeds shown in Fig. 2(a1-c1), the BCC precipitates all show spherical and noodle-like morphology. Compared with the enlarged dark-field illustrations, there is no obvious difference in the size of BCC precipitates, with a diameter of 8-20 nm. In the high-magnification HADDF images and its TEM-EDS maps shown in Fig. 2(a2-c2), Cr gradually enriched in the BCC phase with the decrease of scanning speed, reflecting that the precipitation of BCC phase is a process of spinodal decomposition. With the decrease of scanning speed, the time for circulating heat input by laser to the deposited material will be longer, which promotes the diffusion and enrichment of elements and eventually leads to the formation of BCC precipitation phase.

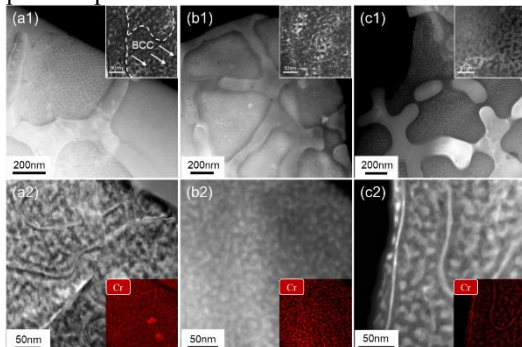


Fig. 2(a1-c1) show the HADDF images and the enlarged DF images of spinodal decomposition at the scanning speed of 1200 mm/s, 1000 mm/s and 800 mm/s respectively; (a2-c2) HAADF images at high magnification and their EDS maps.

Study shows that dendrites and eutectic in eutectic alloys will compete for growth under different undercooling degrees [6]. At lower undercooling, the growth rate of eutectic is the fastest, so a complete eutectic structure can be formed. When the undercooling reaches a certain degree, the growth rate of dendrites exceeds the growth rate of eutectic, and the trend is more obvious with the increase of supercooling. In the rapid solidification

process of laser selective melting, with large undercooling, B2 dendrites grow rapidly and become the main structure in the alloy. When the eutectic transformation volume of the remaining liquid phase is small, and its thickness is equivalent to the eutectic spacing, divorced eutectic may occur [5]. The B2 phase in eutectic is attached to the primary B2 dendrite and continues to grow, while the FCC phase is left alone between dendrites.

4 Conclusion

In this paper, the evolution behavior of the cellular structure of SLM EHEAs is studied by adjusting SLM process parameters. When the laser scanning speed is high, the cooling rate of the molten pool increases, and the size of the cellular structure is refined. With the decrease in scanning rate, the time of cyclic thermal loading of deposited materials by laser is prolonged, which promotes the amplitude modulation decomposition process of the BCC phase in cells.

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