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論 文 内 容 要 旨

Chapter 1. Introduction

Electron beam melting (EBM) is the most advanced 3D printing technology of metal, which can produce any 3D structures with high density (>99.9%) from metal powders by scanning a high-power electron beam to melt metal powder selectively along a series of 2D slices of a 3D object repeatedly, layer by layer. EBM has been attracting wide attention because of its ability to be applied to advanced metal alloys, such as Ni-based superalloys, Co-based alloys, Ti-alloys, for applications such as aerospace engine parts and biomedical orthopedic implants, which are mostly difficult to be formed by conventional processes. However, only limited has been known about the microstructures of EBM-built product, which should greatly affect the properties of the alloys.

Because of the uniqueness of EBM process, in particular, (i) directional solidification by scanning electron beam, and (ii) successive stacking of layered 2D slices, it was anticipated that the microstructure and accordingly the mechanical properties of EBM-built products, depend on its orientation with respect to the electron-scanning direction and the stacking direction (i.e. build direction). Hence, the main purposes of this Ph.D study were to elucidate the build direction dependence of microstructures and the mechanical properties of Ni-based superalloy and Co-based alloy, which are typical alloys at which the EBM is being targeted.

Chapter 2. Literature review of characteristic of electron beam melting

The microstructure of EBM-built object is closely related to the solidification condition of the melt pool, which is affected by processing parameter of EBM, such as beam current, beam focus offset, scanning speed, scanning route and line offset. The

melt pool morphology, temperature gradient and solidification rate at the solid/liquid interface can be obtained by finite element simulation with considering beam power (P) and scanning velocity (V). Based on the solidification map of the material, the P-V process map, which shows the relationship among P, V, and microstructure, can be plotted. Electron beam melting can control the microstructure in wider range than other additive manufacturing processes because of its much wider operation region of absorbed power and scanning velocity for object fabrication.

Chapter 3. Microstructure of Inconel 718 with various build directions

The microstructures of Inconel718 rods fabricated by EBM with cylindrical axes deviating from the build-direction by 0°, 45°, 55°, and 90° were investigated, focusing on the effect of build direction. Single crystal-like structure can be obtained by increasing energy density (via by increasing the beam current and/or by decreasing the line offset) and decreasing the scanning speed to ensure the completely melt of the powders. The cylindrical axes were oriented near <100>, <110>, <111> and <100> directions in samples with angles of 0°, 45°, 55°, and 90°, respectively, as shown in Fig. 1. Precipitate amount decreased along the build height in the as-EBM-built rod because the in-situ aging time decreased with increasing build height, which caused the hardness decreasing with the build height. However, inhomogeneous distribution of precipitates in the build height can be solved by subsequent solution treatment without changing the preferential crystal orientation. Beside (Nb,Ti)(C,B) particles, δ -Ni₃(Nb, Ti) phase and/or Laves phase were aligned along the build direction based on the build condition. The formation of single crystal-like microstructure accompanied with appearance of Laves phase, which was related to the strong segregation of Nb and Mo at grain boundary in high energy density and lower scanning speed.

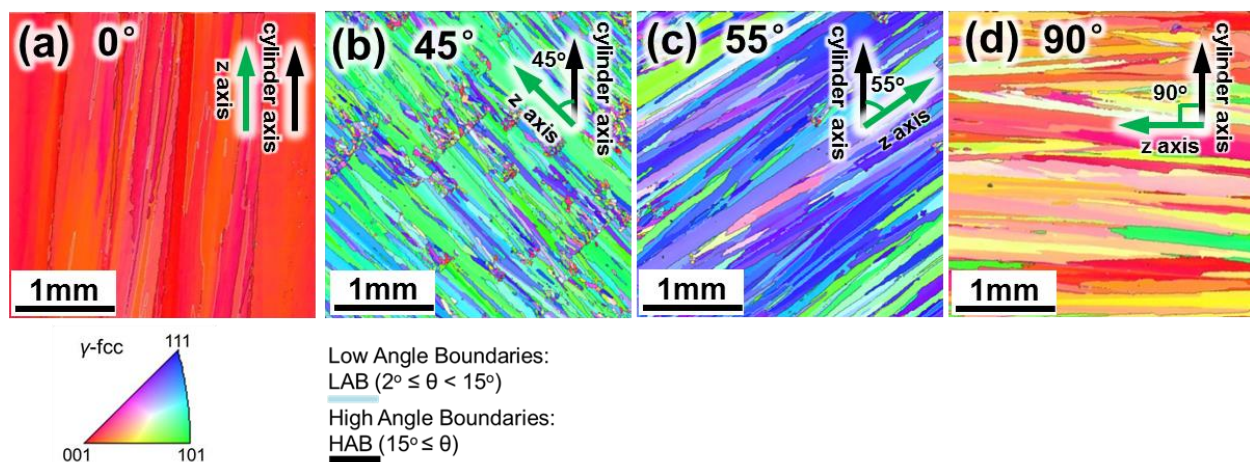


Fig.1. EBSD-IPF maps on the longitudinal cross-section of the top part of as-EBM-built samples. (a) 0°-sample (b) 45°-sample, (c) 55°-, and (d) 90°-sample.

Chapter 4. High temperature mechanical properties of Inconel718 with various build directions

The effect of the build direction on the high temperature mechanical properties of Inconel 718 rods fabricated by EBM with various build directions was investigated with considering the anisotropy of grain boundary, γ' and γ'' arrangement and crystal orientation. Uniform precipitate distribution and higher hardness of the EBM-built rods can be obtained by solution treatment at 1045 °C for 1 h, and first aging treatment at 720 °C for 8 h as well as second aging treatment at 620 °C for 8 h. After this heat treatment, the preferential crystal orientation did not to change significantly. Strength and ductility of EBM-built Inconel 718 alloy can be improved by heat treatment, probably due to the increase of γ'' and γ' and decrease of δ phase. The intrinsic strength of the samples might be hidden by the unmelt particles. However, by comparing the anisotropy of strength of the Inconel 718 built in various directions with those expected from (i) the orientations of grain boundaries, (ii) γ' and γ'' precipitate arrangement, and (iii) crystallographic orientation, the higher strength was expected to be obtained in the order of 55°-sample, 0°- sample, 90°- sample, and 45°-samples.

The creep properties exhibited build direction dependence, as shown in Fig. 2, which can be mostly attributed to the difference in the Schmid factors in the grains with different crystal orientations. 55°-sample (near $\langle 111 \rangle$ orientation) exhibited the smallest creep rate among the samples. The creep rupture time of 0°- and 55°-samples were longer than those of wrought counterparts under the same creep condition. The γ'' variant with c axis parallel to loading axis in 0°-and 90°-sample was found to dissolve into matrix during creep test, which will increase their minimum creep rate significantly.

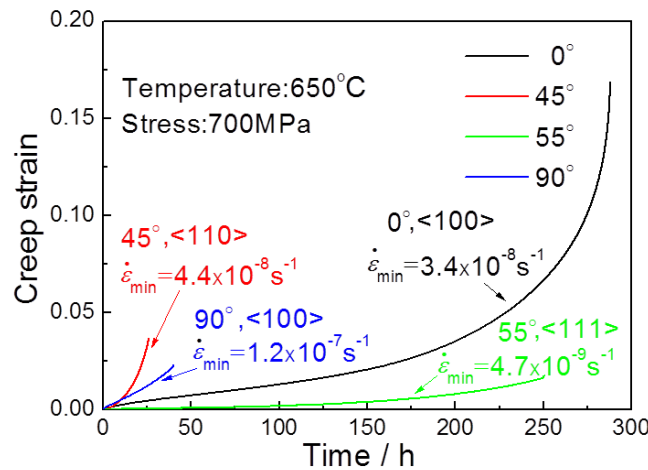


Fig. 2. Creep curves of samples with various build directions at 650 °C with stress of 700 MPa.

Chapter 5. Microstructure of Co-Cr-Mo alloy with various build directions

The microstructures of Co-Cr-Mo alloy rods fabricated by EBM with cylindrical axes deviating from the build-direction by 0°, 45°, 55°, and 90° were investigated, focusing on the effect of build direction. Single crystal-like structure of Co-Cr-Mo alloy with metastable γ -fcc phase can be obtained by the EBM process. The preferential crystal orientations of the γ phase in

the as-EBM-built 0°, 45°, 55°- and 90°-samples along the cylindrical axial directions were near <100>, <110>, <111>, and <100>, respectively. $M_{23}C_6$ precipitates were observed to align along the build-direction with intervals of around 3 μm in all the samples. M was determined to be Cr, Mo, or Si in $M_{23}C_6$. Although constituent phase varied along the build direction in the as-EBM-built rod, from single ε -hcp phase in the bottom to single γ -fcc phase in the top, as shown in Fig. 3, γ -fcc phase can be obtained in a wide range of build height, i.e. approximately 40 mm from the top finishing plane. Displacive (i.e. martensitic) transformation, which holds Shoji–Nishiyama orientation relationship, occurred during the EBM process and resulted in a textured ε phase grains in the EBM-built sample. Larger ε -hcp grains were obtained in the EBM process than in an aging heat treatment with similar thermal history.

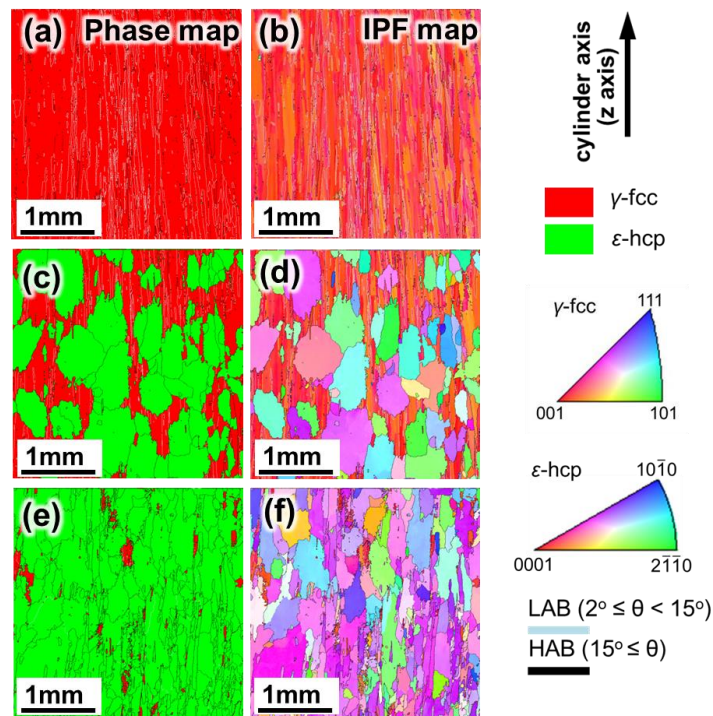


Fig. 3. EBSD Phase maps (a,c,e) and IPF maps (b,d,f) on longitudinal cross-section of different height of as-EBM-built 0°-sample rod, (a,b) top part, (h=79 mm) (c,d) center-bottom part (h= 32mm), and (e,f) bottom part (h=5 mm).

Chapter 6. High temperature mechanical properties of Co–Cr–Mo alloy with various build directions

The high temperature mechanical property of Co–Cr–Mo alloy rods fabricated by EBM with cylindrical axes deviating from the build-direction by 0°, 45°, 55°, and 90° were investigated, with special focus on the effects of anisotropic columnar-grain structure and carbide distribution. The γ -fcc matrix phase could be wholly transformed into ε -hcp phase after aging treatment at 800 °C for 24 h. No significant preferential orientation was recognized in the ε grains of the aged samples. Plate-like M_2N (M =Cr, Mo, or Si) precipitates appeared in the matrix after aging treatment. In the aged rod, the ε -hcp grain size increased along build height at first, then decreased gradually to the phase transformation position of γ -fcc to ε -hcp in the as-EBM-built rod, and

maintained nearly constant in the initial single γ -fcc region. The diffusive phase transformation did not weaken the anisotropy in the mechanical properties notably. 55°-sample exhibited the highest *UTS* of 806 MPa at 700 °C with a strain rate of $1.5 \times 10^{-4} \text{ s}^{-1}$. The extremely low *SFE* and carbide array were the possible reasons for the poor ductility at 700 °C. Basal slip is main deformation mode at the temperature range of 650-800 °C because of the widely expanded Shockley partial dislocation pair. The creep rupture time and steady state creep rate were found to be independent of the build direction because of the occurrence of diffusive transformation after aging treatment as well as the similarly distributed carbide on the slip plane of different ε grains. Fracture tended to occur in fine grain region of the aged rod, which used to be single γ -fcc phase before aging treatment. The creep curves exhibited typical three creep stages at all the investigated temperatures ranging from 650 to 800 °C under the stress ranging from 240 to 330 MPa. The relation between minimum creep rate and applied stress could be described by the constitutive equation. The stress exponent n and apparent activation energy Q were determined to be 5 and 365 kJ mol⁻¹, respectively.

Chapter 7. Conclusions

Single crystal-like structure of fcc based alloy (Inconel718 and Co-Cr-Mo alloy) with $\langle 001 \rangle$ orientation in build direction can be obtained by the EBM process, which suggests crystal orientation can be controlled by selecting the oriented direction relative to the build direction (z axis), thus the mechanical properties can be controlled. Because of the effect of in-situ aging on the early-built part, the microstructure varied along the build height. Therefore, post-built heat treatment is necessary to homogenize the microstructure, with specially considering the thermal history in EBM process.

論文審査結果の要旨

近年、3D プリンターまたは Additive Manufacturing と呼ばれる積層造形技術が、革命的製造技術として注目されている。特に、電子ビーム積層造形 (EBM) やレーザー積層造形 (SLM) 等の金属用積層造形は、人工関節やガスタービン翼等、特に高い耐久性が要求される製品の製造に適用できる工業技術として重要である。一方、金属材料の特性は、結晶粒径、結晶方位分布、析出物のサイズや分布等の組織に強く依存する。しかしながら積層造形で得られる金属材料の組織についての知見が殆どなかった。本論文は、3D 積層造形技術を耐久性や信頼性が求められる製品に適用することを目指し、EBM 造形された (i) 耐熱 Ni 基超合金 (Inconel718) ならびに (ii) 生体医療用 Co-Cr-Mo 合金の金属組織とその特性への影響を解明した研究について記述するものであり、以下の 7 つの章からなる。

第 1 章は緒言であり、様々な積層造形技術の原理、従来研究、研究目的及び意義について述べている。

第 2 章では、積層造形した金属中の組織と熔融池の移動で形成される凝固組織との関係について述べ、(1) 造形物の組織は主にビーム強度と走査速度により制御可能なこと、(2) 他の金属用積層造形と比較して EBM 造形はビーム強度と走査速度を広範に変更でき組織を種々に制御できることを示している。

第 3 章では Inconel718 合金の EBM 造形において、従来知られていた柱状晶組織の形成だけでなく、結晶の方位が、EBM 造形の積層方向及び電子線走査方向に $\langle 100 \rangle$ 方向が強く配向することを、後方散乱電子回折 (EBSD) 法を駆使した詳細な解析により明らかにした。造形物の結晶方位はビーム走査方向と積層方向に対する方向を選択することで制御できることを示した。また、(1) 一方向凝固により析出物が造形方向に沿って整列すること、(2) 凝固後の高温保持中に時効が進み最初に造形した部分の析出物量が多くなること、(3) 造形物全体の組織は造形後の熱処理によって均一できること、等を示している。

第 4 章では、第 3 章の成果を基に、造形方向に対して種々に傾斜させた円柱状試験片を EBM 造形し、それらの高温引張変形挙動が荷重軸の造形方向からの角度に強く依存し、特に造形方向と電子線走査方向の立方対角方向で最大強度が得られることを示した。また、結晶配向に由来した特異なクリープ変形挙動を見出し、それが γ'' 相の安定性に対する荷重軸の影響により説明できることを、透過電子顕微鏡 (TEM) による詳細な解析を基に解明した。

第 5 章では、EBM 造形された Co-Cr-Mo 合金の組織が、造形方向の位置により変化することを、各位置から採取した試料の EBSD 解析により明らかにした。造形初期に熔融凝固した底部では平衡相の ϵ -hcp 相が形成され、上部に近づくにつれ準安定相の γ -fcc 相の体積率が増し、上部半分以上が γ 単相となることを再現性よく示した。さらに、相変態熱処理により γ 単相部には ϵ 相の微細結晶粒が形成されることから、人工関節製造においては人工関節の使用時に高負荷がかかるネック部分を上部となる様に製造することが信頼性向上にとって有効であることを示した。また従来鑄造材では見られなかった、造形方向に沿って炭化物が均一に整列した組織が形成されることも見出した。

第 6 章では、造形方向に対して種々に傾斜させた柱状試験片を熱処理し、それらの高温引張変形とクリープ変形挙動を研究した結果を記述している。特に、拡散相変態によりランダム結晶方位の ϵ -hcp 相が形成され強度の異方性が軽減されること、 ϵ -hcp 相は高温で極めて低い積層欠陥エネルギーを有し Shockley 部分転位対の運動が強く底面すべりに拘束されるために高温でも低い塑性変形能を示すこと、クリープ破壊が EBM 材中の不均一組織の中でも常に微細結晶粒部分で発生すること等も明らかにした。

第 7 章は結論であり、研究で得られた知見を総括するとともに、今後の展望について述べている。

以上のように、本論文は EBM 造形された Inconel718 合金と Co-Cr-Mo 合金の組織とその特性への影響を解明しており、積層造形技術の発展と新材料の創製に貢献し、工学に大きく寄与するものといえる。よって、本論文は博士(工学)の学位論文として合格と認める。