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Additive manufacturing of $MoSi_2$ and $NbSi_2$ products for ultrahigh-temperature structural materials

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Transition metal disilicides such as $C11_b$-$MoSi_2$ and C40-$NbSi_2$ are promising candidates for ultrahigh-temperature structural materials aiming at the use over 1200°C. However, their product fabrication has been limited owing to their significant brittleness. To overcome this, we have tried the additive manufacturing (AM) of their products via selective laser melting. As a result, we have succeeded their shape control by the appropriate selection of process parameters. In addition, strong texture control was achieved in them. It is to note here that the crystallographic features of the developed texture wer e different from those observed in cubic materials such as Ni-based superalloys and beta-Ti for biomedical implant. By the unidirectional scanning of the laser (X-scan), single crystalline texture in which [001] is aligned along the scanning direction could be developed in $MoSi_2$, which possibly results in the fabrication of the products with better high-temperature strength. However, in the directional scanning with a subsequent rotation of 90° for each layer (XY-scan), only fiber-like texture in which <100] is weakly aligned along the building direction was developed. In case of $NbSi_2$, on the other hand, the development of the so-called basal fiber texture wherein <0001> was parallel to the building direction was achieved in any scanning strategies, and the single crystalline texture was not developed. The $C11_b$-$MoSi_2$ and C40-$NbSi_2$ have the tetragonal and hexagonal unit cell, respectively. A comparison of these results led us to the conclusion that crystal symmetry, i.e., the multiplicity of the preferential crystal growth direction, is one of the primary factors that governs the features of the textures developed in AM-built materials.

1. Introduction

There is a strong demand that the development of the material that can tolerate the use over 1200 °C, i.e. at higher temperatures than that the Ni-based superalloys can be used. Transition-metal disilicides have been significantly focused as promising candidates as such ultra-high-temperature structural materials. Among the transition metal disilicide, $MoSi_2$ is one of the most promising candidates because of its high melting temperature, good oxidation resistance, relatively low density and high thermal conductivity [1–4]. $MoSi_2$ crystallizes in the $C11_b$ structure, which is based on a tetragonal unit cell. Because of its relatively high crystal symmetry, many slip systems such as {110)<111], {011)<100], {010)<100], {023)<100], and {013)<331] can be operative [1,4]. (The mixed notation {hkl) and <uvw] is used to differentiate the first two indices from the third index which does not play the same role as the first two because of the tetragonality of $C11_b$-$MoSi_2$.) It is reported that the $MoSi_2$ shows the plastic deformability to some extent even at room temperature [4].

As another candidate, silicides having the hexagonal C40 structure are focused for such structural applications [3,5]. Four transition-metals, V, Cr, Nb and Ta, are known to form binary C40 disilicides with Si. Of these C40 disilicides, $NbSi_2$ is the most promising on the viewpoint of their melting points and densities. $NbSi_2$ is expected to show high strength by the control of texture, since only the (0001)<1120> basal slip is predominantly operative. In addition, yield stress anomaly appears at high temperatures around 1400 ºC [5]. Therefore, the development of C40/$C11_b$ oriented two-phase lamellar crystal has also been recently proceeded by using the Mo-oversaturated C40-phase single phase crystal as a starting material, to improve the fracture toughness and high temperature strength [6-9].

As the common critical problem for those disilicides, however, they show a low workability owing to its significant brittleness. Additive manufacturing (AM) has attracted considerable interest for the noble manufacturing process for such brittle materials. AM allows for the production of complex geometries as a net shape, which cannot be accomplished with standard manufacturing techniques such

as casting or forming. In addition, AM does not require expensive molds or dies, which potentially reduces the cost for small runs. Thus, the application of AM is strongly desirable for those silicides. To the best of our knowledge, however, there had been no reports of the fabrication of $MoSi_2$ and $NbSi_2$ products by AM processes. In this presentation we report a strategy for fabricating those silicide samples by AM using an improved process [10, 11]. In addition, we describe how to control the texture during the AM process, which has a strong possibility of improving the high-temperature strength of silicides [12].

2. Experimental procedure

The $MoSi_2$ and $NbSi_2$ powders were supplied by JAPAN New Metals Co., LTD., Japan. A prealloyed ingot was pulverized to obtain a powder. Using the powder, cubic-shaped samples with dimensions of 10 mm × 10 mm × 10 mm were manufactured by utilizing a laser powder bed fusion (L-PBF) method in an argon atmosphere by using EOS M 290, EOS, Germany. In the L-PBF process, the laser power, scan pitch, layer thickness, and scan speed were variously changed to clarify the appropriate fabrication condition. The laser was basically scanned bidirectionally (zigzag) in one direction (X-scan). In addition, bidirectional scanning with a subsequent rotation of 90° for each layer (XY-scan) and scanning with a subsequent rotation of 67° (Rot-scan) were additionally performed to examine the variation in the crystallographic texture depending on the scanning strategy.

Electron backscattering diffraction (EBSD) analysis in a scanning electron microscope (SEM, JSM-6500F, JEOL, Japan) and X-ray diffraction (XRD, RINT-2500V, Rigaku, Japan) analysis using Cu-Kα radiation were utilized to examine the texture of the samples. The concentration distribution in the fabricated samples was examined by energy-dispersive X-ray spectroscopy (EDS) in the SEM.

3 Results and discussion

By selecting the appropriate process parameter, we succeeded in fabrication the dense L-PBF products with high strength (Vickers hardness). In case of the fabrication of $MoSi_2$, control of the thermal expansion coefficient of the start plate for AM was found to be important for building a three-dimensional $MoSi_2$ product to reduce the mismatch between them [11].

The development of strong texture was confirmed in the fabricated products. In the investigation of the texture in those products, we found that their characteristic features and formation mechanisms are different from those known in conventional materials such as bcc-Ti and fcc-Ni-based superalloy [13,14].

In bcc-Ti, different single-crystalline textures in which <011> and <100> were aligned along the building direction were developed using the X-scan and XY-scan strategies. However, the features of the texture for tetragonal $MoSi_2$ and hexagonal $NbSi_2$ were different. In tetragonal $MoSi_2$, a single crystalline texture was developed in the X-scan sample, in which the z-building and x-scanning directions were parallel to [001] and <100], respectively. However, only a fiber-like texture where the z-building direction was parallel to <100] was developed, and a single-crystalline texture was not developed in the XY-scan sample. By contrast, only a fiber-like texture in which [0001] was parallel to the z-building direction was developed in both the X- and XY-scan samples in hexagonal $NbSi_2$. Those texture developments are effective to improve the high temperature strength including creep resistance, taking the operative slip systems in them into consideration.

Fig. 1 shows the summary for the characteristics of the texture. The different texture evolution features were derived from the difference in crystal symmetry, which affected the "multiplicity" of the preferential growth direction in them.

The $C11_b$ structure in $MoSi_2$ contains a tetragonal unit cell, wherein three bcc lattices are stacked along the c-axis. The preferential growth direction of the elongated cells in $MoSi_2$ was parallel to <100]. In the L-PBF of $MoSi_2$, the growth of the columnar cells occurred primarily in the plane perpendicular to the x-scanning direction in samples with a strong texture. Hence, in the X-scan sample, the preferential growth of the cells parallel to <100] and the subsequent lateral growth parallel to <010] occurred in the yz-section because the [100] and [010] directions were crystallographically equivalent in the tetragonal crystal. Consequently, [001], which is perpendicular to both [100] and [010], aligned along the x-scanning direction. Hence, a single-crystalline texture was developed, similar to the fcc and bcc materials.

In the case of the XY-scan in $MoSi_2$, however, the crystal orientations in the first X-scan and the following Y-scan regions could not be matched, unlike the cases in the fcc and bcc materials. This is because the a-axis and c-axis were not crystallographically equivalent in tetragonal $C11_b$-$MoSi_2$. Hence, a single-crystalline texture could not be developed for $C11_b$–$MoSi_2$ in the XY-scan, and only a weak fiber texture, wherein the <100] cell growth direction was parallel to the z-building direction, was developed in the XY-scan sample.

In the L-PBF of hexagonal-$NbSi_2$, the preferred cell growth direction was <0001>. It is noteworthy that the <0001> is only one direction in the unit cell of the hexagonal crystal. This differs from the <100> in cubic materials, wherein the three directions are parallel to <100>. Furthermore, this differs from the <100] in the tetragonal $C11_b$–$MoSi_2$, wherein the two directions are parallel to the <100] in the unit cells, denoted by the crystallographic multiplicity, shown in Fig. 1 with red arrows. Hence, during the growth process of the elongated cells in $NbSi_2$, the primary elongation direction was parallel to <0001>, but the subsequent lateral growth (secondary growth) direction in the yz-section was arbitrary because only one <0001> axis existed in the hexagonal crystal. Therefore, a single-crystalline texture was absent, and a fiber-like texture developed, wherein only <0001> was parallel to the building direction in hexagonal $NbSi_2$. This occurred similarly in the XY-scan. Hence, no significant changes were observed in the texture of the samples. It is noteworthy that a similar texture formation was reported in a hexagonal close-packed Mg alloy [15].

4. Conclusions

We have first succeeded in fabricating the $MoSi_2$ and $NbSi_2$ samples via L-PBF, by tuning-up the appropriate process parameters. In the fabricated samples, texture development was confirmed, that are suitable for ensuring the high temperature strength including creep

resistance, taking the operative slip systems in them into consideration.

By the comparison of the results with cubic fcc and bcc materials and tetragonal $C11_b$-$MoSi_2$ and hexagonal C40-$NbSi_2$, it was found that the crystal symmetry in the material, i.e. the multiplicity of the preferential growth direction, is one of the strong factors that govern the developing feature of the texture in the AM process.

3. Boettinger W.J., Perepezko J.H. and Frankwicz P.S., "Application of ternary phase diagrams to the development of $MoSi_2$-based materials", Mater. Sci. Eng., A, Vol.155, pp.33-44, 1992.
4. Ito K., Inui H., Shirai Y. and Yamaguchi M., "Plastic deformation of $MoSi_2$ single crystals", Philos. Mag., A, Vol.72, pp. 1075-1097, 1995.
5. Nakano T., Kishimoto M., Furuta D. and Umakoshi Y., "Effect of substitutional elements on plastic behaviour of $NbSi_2$ based silicide single crystals with C40 structure", Acta Mater., Vol.48, pp.3465-3475, 2000.

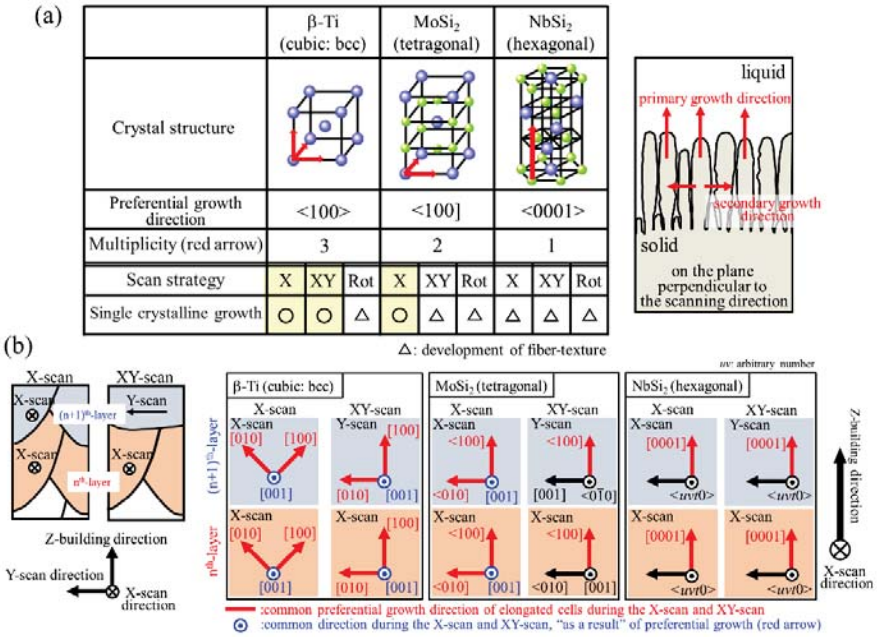

Fig. 1 (a) Relationship among crystal structure, preferential growth direction of elongated cell, and texture developed in L-PBF. (b) Schematic illustration of variations in developing features of texture with crystal structures during X-scan and XY-scan processes in cubic (bcc) Ti–15Mo–5Zr–3Al, tetragonal $MoSi_2$, and hexagonal $NbSi_2$. Figure was reproduced from [12], under the terms of the Creative Commons CC-BY license.

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REFERENCES

1. Umakoshi Y., Sakagami T., Hirano T. and Yamane Y., "High temperature deformation of $MoSi_2$ single crystals with the $C11_b$ structure", Acta Metall. Mater., Vol.38, pp.909-915, 1990.
2. Vasudevan A.K. and Petrovic J.J., "A comparative overview of molybdenum disilicide composites", Mater. Sci. Eng., A, Vol.155, pp.1-17, 1992.
6. Nakano T., Nakai Y., Maeda S. and Umakoshi Y., "Microstructure of duplex-phase $NbSi_2$(C40)/$MoSi_2$($C11_b$) crystals containing a single set of lamellae", Acta Mater., Vol.50, pp.1781-1795, 2002.
7. Nakano T., Hagihara K., Nakai Y. and Umakoshi Y., "Plastic deformation behavior of $NbSi_2$/$MoSi_2$ crystals with oriented lamellae", Intermetallics, Vol 14, pp.1345-1350, 2006.
8. Hagihara K., Hama Y., Yuge K. and Nakano T., "Misfit strain affecting the lamellar microstructure in $NbSi_2$/$MoSi_2$ duplex crystals", Acta Mater., Vol.61, pp. 3432-3444, 2013.
9. Hagihara K., Araki H., Ikenishi T., Nakano T., "Creep-deformation behavior of $(Mo_{0.85}Nb_{0.15})Si_2$ lamellar-structured C40/$C11_b$ two-phase crystals", Acta Mater., Vol.107, pp.196-212, 2016.

10. Hagihara K., Nakano T., Suzuki M., Ishimoto T., Suyalatu and Sun S.-H., "Successful additive manufacturing of $MoSi_2$ including crystallographic texture and shape control", Jour. Alloys Compo., Vol.696, pp.67-72, 2017.
11. Hagihara K., Ishimoto T., Suzuki M., Ozasa R., Matsugaki A., Wang P. and Nakano T., "Factor which governs the feature of texture developed during additive manufacturing; clarified from the study on hexagonal C40-$NbSi_2$", Scripta Materialia., Vol.203, pp.114111, 2021.
12. Hagihara K. and Nakano T., "Control of anisotropic crystallographic texture in powder bed fusion additive manufacturing of metals and ceramics - a review", Journal of Metals (JOM)., Vol.74, pp.1760-1773, 2022.
13. Ishimoto T., Hagihara K., Hisamoto K., Sun S.-H. and Nakano T., "Texture control of beta-type Ti–15Zr–5Mo–3Al alloy by selective laser melting for the development of novel implants with an extremely low Young's modulus", Scripta Mater., Vol.132, pp.34-38, 2017.
14. Sun S.H., Hagihara K. and Nakano T., "Effect of scanning strategy on texture formation in Ni-25at.%Mo alloys fabricated by selective laser melting", Mater. Design, Vol.140, pp.307-316, 2018.
15. Esmaily M., Zeng Z., Mortazavi A.N., et al., "A detailed microstructural and corrosion analysis of magnesium alloy WE43 manufactured by selective laser melting", Addit. Manuf., Vol.35, pp. 101321, 2020.