



# HOKKAIDO UNIVERSITY

|                  |                                                                                                                                                            |
|------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Title            | Hall-Petch strengthening of an Fe-C-Cr-Ni eutectic alloy under additive manufacturing conditions                                                           |
| Author(s)        | Matsuura, Kiyotaka; Saito, Genki; Sakaguchi, Norihito et al.                                                                                               |
| Citation         | Journal of Alloys and Compounds, 1043, 184213<br><a href="https://doi.org/10.1016/j.jallcom.2025.184213">https://doi.org/10.1016/j.jallcom.2025.184213</a> |
| Issue Date       | 2025-10-11                                                                                                                                                 |
| Doc URL          | <a href="https://hdl.handle.net/2115/96165">https://hdl.handle.net/2115/96165</a>                                                                          |
| Rights(URL)      | <a href="https://creativecommons.org/licenses/by-nc/4.0/">https://creativecommons.org/licenses/by-nc/4.0/</a>                                              |
| Type             | journal article                                                                                                                                            |
| File Information | J. Alloy. Compd. 1043_184213.pdf                                                                                                                           |





# Hall-Petch strengthening of an Fe-C-Cr-Ni eutectic alloy under additive manufacturing conditions

Kiyotaka Matsuura<sup>a,d,\*</sup>, Genki Saito<sup>b</sup>, Norihito Sakaguchi<sup>a</sup>, Naomi Kitagawa<sup>c</sup>, Paweł Rutkowski<sup>d</sup>, Dariusz Kata<sup>d</sup>

<sup>a</sup> Faculty of Engineering, Hokkaido University, Kita 13 Nishi 8, Kita-ku, Sapporo 060-8623, Japan

<sup>b</sup> Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

<sup>c</sup> Research and Development Center, Mitsubishi Steel MFG. Co., Ltd., 1-6 Yawata Kaigandori, Ichihara, Chiba 290-0067, Japan

<sup>d</sup> Faculty of Materials Science and Ceramics, AGH University of Krakow, al. Mickiewicza 30, Cracow 30-059, Poland

## ARTICLE INFO

### Keywords:

Rapid solidification  
Eutectic particles  
Chromium carbide  
Interparticle distance  
Hall-Petch law  
Additive manufacturing

## ABSTRACT

This paper deals with Hall-Petch strengthening of an Fe-based eutectic alloy that is applicable to the additive manufacturing. This alloy consists of a dual-phase structure of a  $\gamma$ -Fe (Ni) matrix and  $\sim 20$  vol% of eutectic chromium carbide rods. The distance between the eutectic carbide rods or rod spacing was varied over a wide range from  $\sim 10^1$  to  $\sim 10^{-2}$   $\mu\text{m}$  by varying cooling rate during solidification from  $\sim 10^{-1}$  to  $\sim 10^7$   $^\circ\text{C/s}$ . This wide variety of the cooling rate was provided by a variety of cooling methods of the liquid alloy, including slow furnace cooling of the liquid in an alumina crucible, arc melting and fast cooling of a button-like small ingot in a graphite crucible, rapid cooling of small melt pools formed on the surface of the ingot samples using a TIG welder, and extremely rapid cooling of fine melt pools formed on the surface of the ingot samples using a laser scanner. As the rod spacing decreased from  $\sim 10^1$  to  $\sim 10^{-2}$   $\mu\text{m}$ , Vickers hardness of the as-solidified alloy increased from  $\sim 300$  to  $\sim 600$  HV. This considerable increase in hardness was due to the Hall-Petch effect, and the relation between the Vickers hardness,  $HV$ , and the rod spacing,  $\lambda$ , was described as a regression equation of  $HV = 67.4 \lambda^{-1/2} + 305$  with a high correlation coefficient of  $R^2 = 0.9009$ . When this alloy was applied to the laser powder bed fusion, the as-built prototype exhibited a high Vickers hardness of  $\sim 720$  HV, more than twice that of Inconel 718 Ni-based superalloy produced using the same process.

## 1. Introduction

Ni-based superalloys are widely used in various kinds of industries such as aerospace and automotive industries [1,2], due to their excellent mechanical and chemical properties [3,4]. However, they are quite expensive because of the extremely high price of nickel. If the Ni content of the alloys can be reduced with the excellent properties remained, it will lead to reduction of the production cost of the alloys, and such cost-efficient materials will be more widely used in more kinds of industries.

There are many kinds of Fe-based high-strength alloys containing low concentrations of Ni compared with Ni-based alloys, and the strengthening strategy of these Fe-based alloys generally involves plastic deformation and/or heat treatment [5–7]. In the present study, in contrast, we are developing a new Fe-based high-strength alloy that can be used in as-solidified state without plastic deformation, like precise castings and additive manufacturing products.

Generally, the finer the solidification structure, the higher the mechanical strength of the as-solidified alloy [8]. However, as-built Inconel 718 alloy processed by the laser powder bed fusion exhibits low Vickers hardness of only 280–350 HV, in spite of an extremely small inter-dendritic spacing of less than 1  $\mu\text{m}$  [9]. The reason for this is considered to be epitaxial growth at the interface between melt pools during the additive manufacturing process. In general casting processes, the inter-dendritic spacing determines the grain size due to the inhomogeneous nucleation and growth of dendrite crystals [10]. In additive manufacturing processes, however, the melt pool formed by the laser beam partially melts the formerly solidified melt pool and epitaxially solidifies on the solid/liquid interface, which leads to the formation of a huge grain structure despite a fine dendrite structure [11,12]. Therefore, in conventional alloys that form dendritic solidification structures during additive manufacturing, the Hall-Petch strengthening cannot be expected.

In the present study, we thought that if an alloy in which slip

\* Corresponding author at: Faculty of Engineering, Hokkaido University, Kita 13 Nishi 8, Kita-ku, Sapporo 060-8623, Japan.

<https://doi.org/10.1016/j.jalcom.2025.184213>

Received 16 July 2025; Received in revised form 20 September 2025; Accepted 4 October 2025

Available online 9 October 2025

0925-8388/© 2025 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC license (<http://creativecommons.org/licenses/by-nc/4.0/>).

**Table 1**

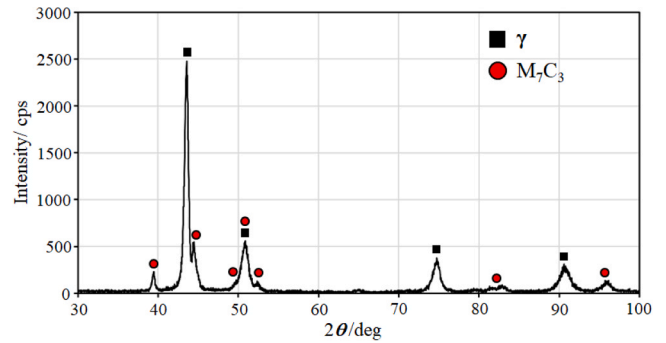
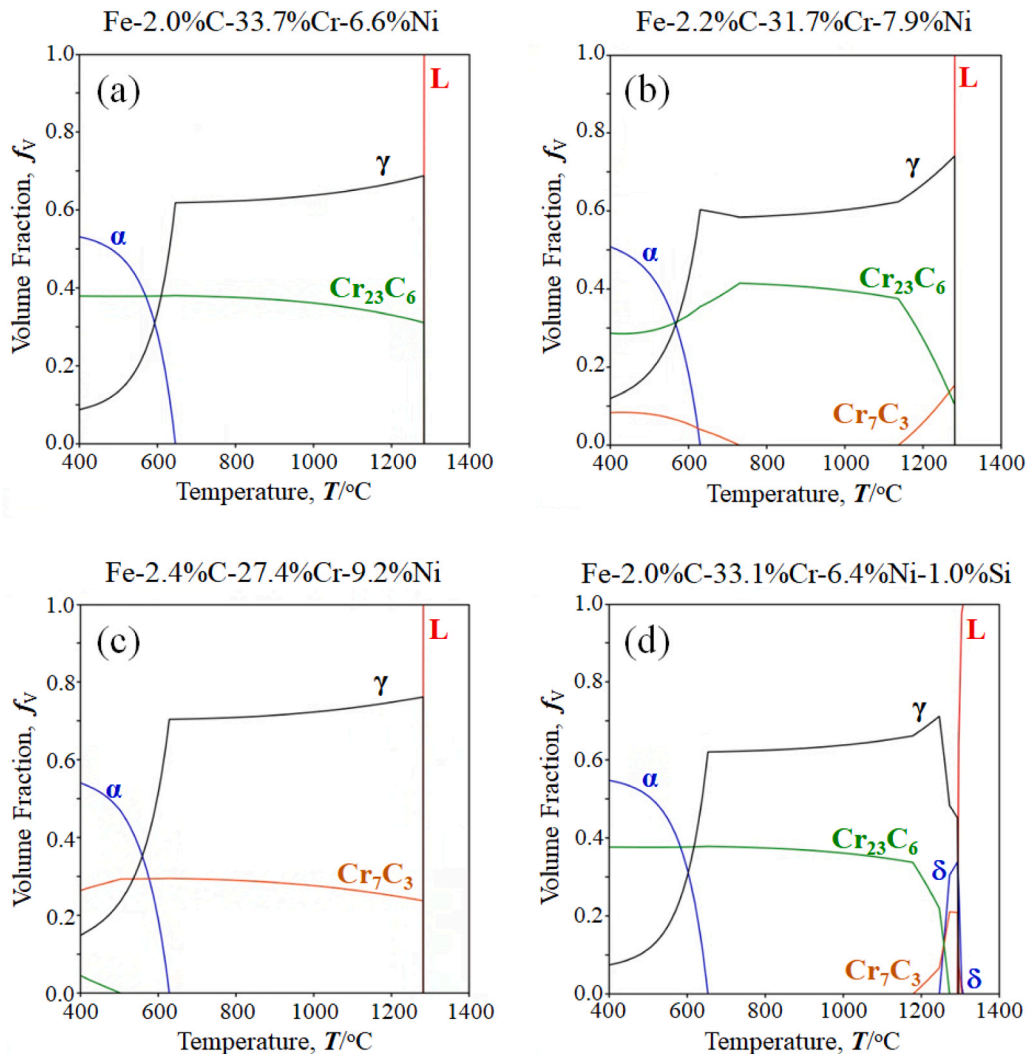
Dimensions and cooling rates of samples.

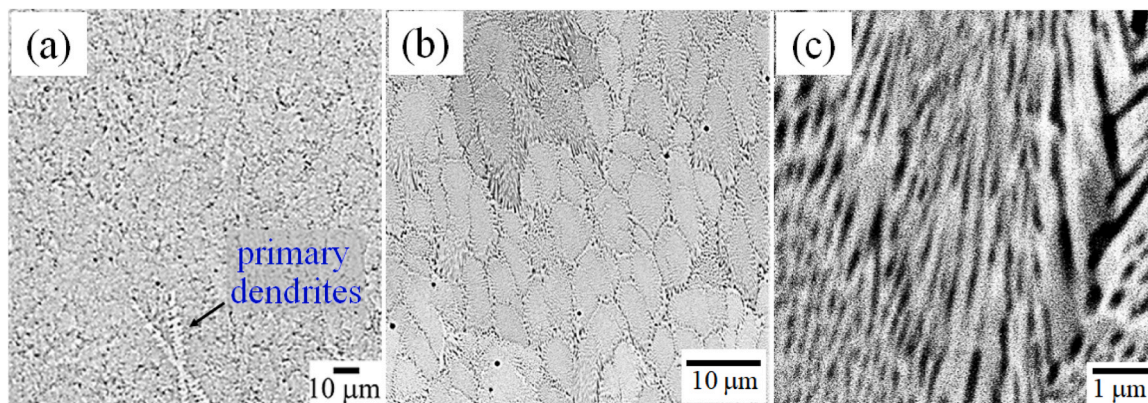
| Samples              | Dimension (mm)                     | Cooling Rate (°C/s)        |
|----------------------|------------------------------------|----------------------------|
| Furnace-melted Ingot | $\phi 20 \times h 15$              | $2 \times 10^{-1}$         |
| Arc-melted Ingot     | $\phi 10 \times t 6$               | $\sim 10^2$                |
| Arc-melted Pool      | $\phi 3-6 \times d 2-4$            | $\sim 10^4$ to $\sim 10^5$ |
| Laser-melted Pool    | $l 1.5 \times w 0.2 \times d 0.15$ | $\sim 10^6$ to $\sim 10^7$ |

deformation can be prevented at the phase boundaries of the multiphase structure could be manufactured using additive manufacturing, the as-built product would exhibit significantly high strength due to the extremely small phase boundary spacing. In order to verify this idea, we melted an Fe-C-Cr-Ni quaternary eutectic alloy consisting of the  $\gamma$ -Fe (Ni) matrix and chromium carbide rods, and solidified the alloy at various cooling rates ranging between  $10^{-1}$  to  $10^7$  °C/s to vary rod spacing (the distance between the chromium carbide rods) ranging between  $10^1$ – $10^{-2}$   $\mu\text{m}$ , and we investigated the relationship between the rod spacing and Vickers hardness. One will see that when the present eutectic alloy has an ultrafine solidification structure, such as in additively manufactured products, it exhibits more than twice the hardness of additively manufactured Inconel 718 superalloy.

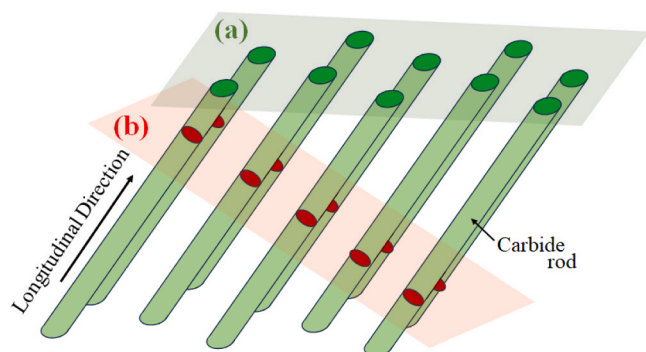
## 2. Experimental procedure

First of all, we performed phase diagram calculations to determine the chemical composition of the Fe-C-Cr-Ni quaternary eutectic alloy to be used in the present study, using the Thermo-Calc software (version 2024) and the TCFE9 database. After determining the alloy composition, we made small ingot samples from raw materials of a commercial granular chromium with a purity of 99.9 mass% and a diameter of

**Fig. 2.** Results of XRD analysis of the furnace-melted sample.**Fig. 1.** Equilibrium phase diagrams of (a) Fe-2.0 %C-33.7 %Cr-6.6 %Ni (mass%) alloy, (b) Fe-2.2s%C-31.7 %Cr-7.9 %Ni (mass%) alloy, (c) Fe-2.4 %C-27.4 %Cr-9.2 %Ni (mass%) alloy, and (d) Fe-2.0 %C-33.1 %Cr-6.4 %Ni-1.0 %Si (mass%), calculated using Thermo-Calc.



**Fig. 3.** Solidification structure images of an arc-melt pool of  $\sim 6$  mm in diameter, showing (a) a few small primary dendrites, (b) fine eutectic colonies and (c) rod-like eutectic structure in the colonies.



**Fig. 4.** Schematic illustration of the cross section of the rod-like eutectic structure. (a) An arbitrary cross section, where the thickness of the carbide rod is partially considerably thin, which leads to inaccurate results of STEM-EDS analysis and overestimate of the volume fraction of the carbide when the area fraction is measured based on the STEM-EDS analysis results. (b) A cross section perpendicular to the longitudinal direction of the rods, where there are no such problems.

$\sim 3$  mm, a commercial nickel wire with a purity of 99 mass% and a diameter of 2.0 mm, and a commercial cast iron rod with a composition of Fe-3.35mass%C-1.67mass%Si and a diameter of  $\sim 25$  mm. The ingot samples were made by two different methods: one was arc melting of raw materials using a TIG welder (YC-200TR6, Panasonic) with an Ar shield gas atmosphere followed by cooling of the melted alloy in a graphite crucible using the Ar cooling gas, and the other was remelting of the arc-melted samples in an alumina crucible using an electric furnace with an Ar atmosphere followed by controlled cooling of the remelted alloy at a constant rate of  $0.2$  °C/s.

The arc-melted sample had a button-like shape with dimensions of  $\sim 10$  mm in diameter and  $\sim 6$  mm in thickness, while the furnace-melted sample had a cylindrical shape with dimensions of  $\sim 20$  mm in diameter and  $\sim 15$  mm in height. The cooling rate of the arc-melted button-like sample was estimated to be  $\sim 10^2$  °C/s based on temperature measurement using a radiation thermometer. The solidification structure of the arc-melted sample will be quite fine compared with the furnace-melted sample due to the quite high cooling rate compared with the controlled cooling rate of  $0.2$  °C/s. In order to add samples with more refined solidification structures, we made small melt pools with a diameter of  $\sim 3$  to  $\sim 6$  mm and a depth of  $\sim 1$  to  $\sim 3$  mm by giving a short-time arc discharge on the surface of both the button-like and cylindrical cold ingots using the TIG welder mentioned above. The TIG arc discharge was performed under conditions of 10 V, 10 A and 1–2 s, in voltage, direct current and discharge time, respectively. The cooling rate of the arc-melt pools was estimated to be  $\sim 10^4$  to  $\sim 10^5$  °C/s based on a relationship

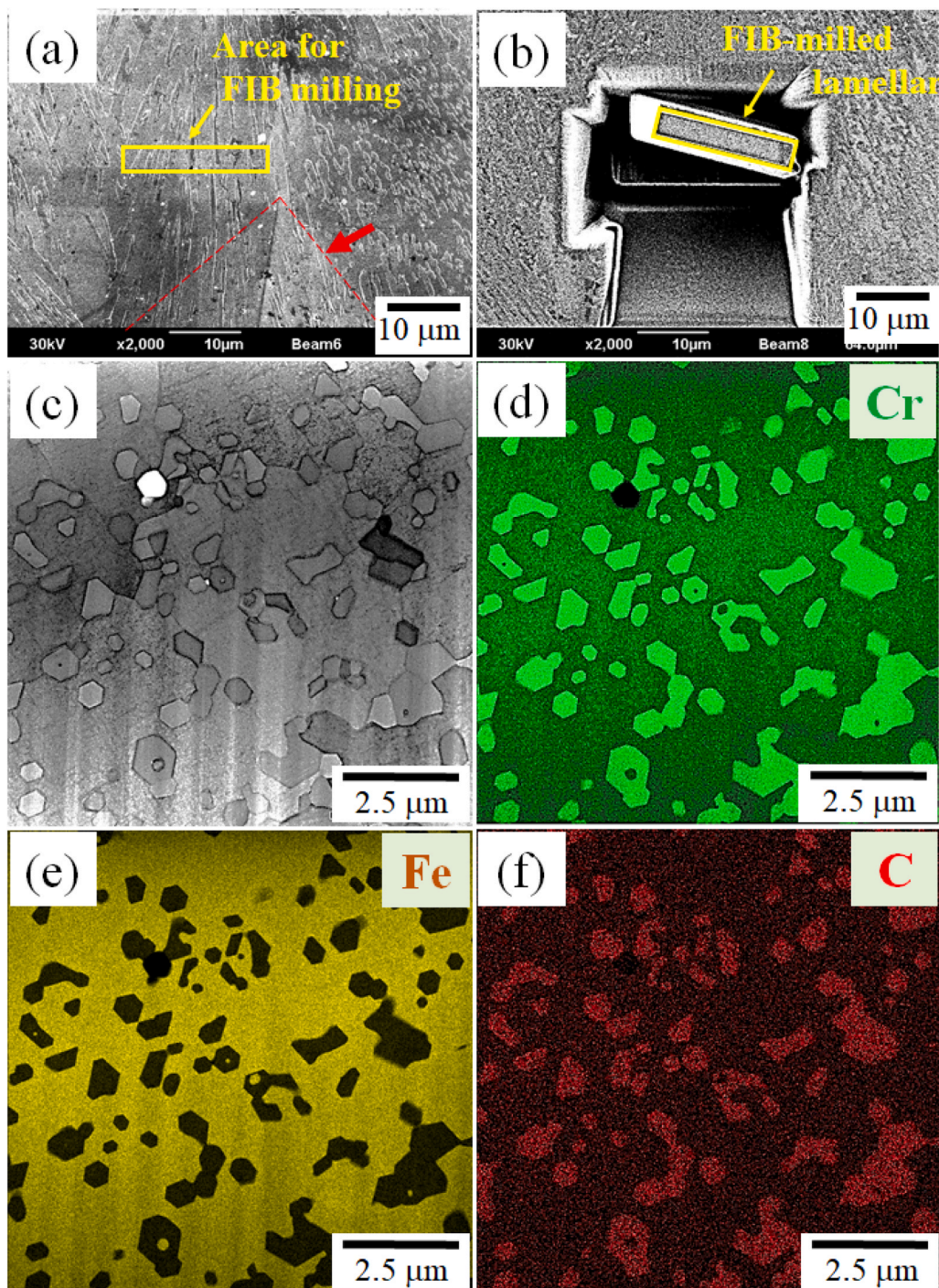
between secondary dendrite arm spacing and cooling rate [14]. We also made much smaller melt pools with a width of  $\sim 200$   $\mu\text{m}$ , a depth of  $\sim 150$   $\mu\text{m}$  and a length of  $\sim 1.5$  mm by giving a laser scan on the surface of the furnace-cooled ingot in an Ar atmosphere using a laser scanner (JK200FL of JK Lasers a GSI Group Company, hurrySCAN 30 of SCAN-LAB) with a CW (Continuous Wave) operating mode. The laser scan was performed under conditions of 200 W in power, 50 mm/s in scan speed and 40  $\mu\text{m}$  in spot diameter. The formation of the melt pool was repeated at 40  $\mu\text{m}$  intervals to make a square scan mark of 4 mm in side length on the surface of the ingot. The cooling rate of the laser-melt pools was estimated to be  $\sim 10^6$  to  $\sim 10^7$  °C/s based on experimental results [15]. The solidification structure of the laser-melt pools will be much more refined due to the much higher cooling rate. The difference in cooling rate depending on the sample preparation method is summarized in Table 1. For comparison purpose, we made another sample of Inconel 718 Ni-based superalloy with a cubic shape of 40 mm in edge length by the laser powder bed fusion process (EOS M 290, EOS GmbH). The laser powder bed fusion was performed in an Ar gas atmosphere under conditions of 350 W in laser power,  $\sim 900$  mm/s in scan speed,  $\sim 200$   $\mu\text{m}$  in spot diameter,  $\sim 70$   $\mu\text{m}$  in scan interval and  $\sim 50$   $\mu\text{m}$  in thickness of the powder bed with a powder diameter of  $\sim 10$   $\mu\text{m}$ .

The microstructures of the ingot samples and the melt pool areas formed on the surface of the ingot samples were observed by using OM, SEM (Phenom ProX, Thermo Fisher Scientific) and STEM (NEOARM, JEOL). An analysis using X-ray diffraction (XRD, Ultima IV, Rigaku) with Cu K $\alpha$  radiation (1.54056 nm in wavelength) was performed to identify the phases existing in the alloy samples at room temperature. A Vickers hardness tester (FM-300e, FUTURE-TECH) was used with an applied load between 0.05 and 1.00 kg to measure the hardness of the carbide phase, the matrix phase and the eutectic area consisting of the mixture of the carbide and matrix phases. The distance between the eutectic carbide rods or rod spacing was measured inside or near the Vickers indentation marks, and the relation between the rod spacing and the hardness of the eutectic area was investigated.

### 3. Results and discussion

Three eutectic compositions were found through phase diagram calculations, as shown in Figs. 1(a) to 1(c). Liquid alloy solidifies into  $\gamma$ -Fe and a chromium carbide at the same time. The type of chromium carbide changes from  $\text{Cr}_{23}\text{C}_6$  to  $\text{Cr}_7\text{C}_3$ , as C and Ni concentrations increase and Cr concentration decreases. In the alloy with an intermediate composition (Fig. 1(b)), the  $\text{Cr}_7\text{C}_3$ -type carbide is produced during the eutectic solidification, and it changes into the  $\text{Cr}_{23}\text{C}_6$ -type carbide during cooling after solidification. Because the alloy presented in Fig. 1(a) has the highest volume fraction of the eutectic carbide, we chose this alloy as the sample to be used in the present study, and we made samples





**Fig. 5.** Microstructure images of the melt pool sample showing (a) an area selected for FIB milling in a colony of the rod-like eutectic structure near a Vickers indentation mark indicated by a red arrow, (b) an FIB-milled lamellar, (c) a STEM image of the FIB-milled lamellar, (d), (e) and (f) STEM-EDS mapping results of Cr, Fe and C, respectively.

from the raw materials as described in the Experimental procedure section. The chemical composition of the samples made was Fe-2.0 %C-33.1 %Cr-6.4 %Ni-1.0 %Si (mass%). Based on this composition, we recalculated the equilibrium phase diagram, and depicted the results in Fig. 1(d). According to Fig. 1(d),  $\delta$ -Fe is formed as the primary solid phase followed by the formation of the secondary solid phase of  $\text{Cr}_7\text{C}_3$ . When a eutectic solidification of  $L \rightarrow \gamma + \text{Cr}_7\text{C}_3$  occurs at 1293°C, the volume fraction of  $\text{Cr}_7\text{C}_3$  increases to 21.0 %. The  $\delta$ -to- $\gamma$  transformation proceeds during cooling after the eutectic solidification, and it is accelerated when the type of the chromium carbide changes from  $\text{Cr}_7\text{C}_3$

to  $\text{Cr}_{23}\text{C}_6$ . The final equilibrium structure of this alloy after cooling to room temperature will consist of  $\alpha$ -Fe,  $\gamma$ -Fe and  $\text{Cr}_{23}\text{C}_6$ , based on the equilibrium phase diagram of Fig. 1(d).

In order to identify the phases existing in the sample at room temperature, we performed an XRD analysis using a furnace-melted sample. The results shown in Fig. 2 reveal that the sample is composed of  $\gamma$ -iron and  $\text{M}_7\text{C}_3$ -type chromium carbide, which means that although the  $\delta$ -to- $\gamma$  transformation occurred, the  $\gamma$ -to- $\alpha$  transformation did not occur during cooling, and the  $\text{M}_7\text{C}_3$  type eutectic chromium carbide remained at room temperature without transforming into  $\text{M}_{23}\text{C}_6$  type, contrary to



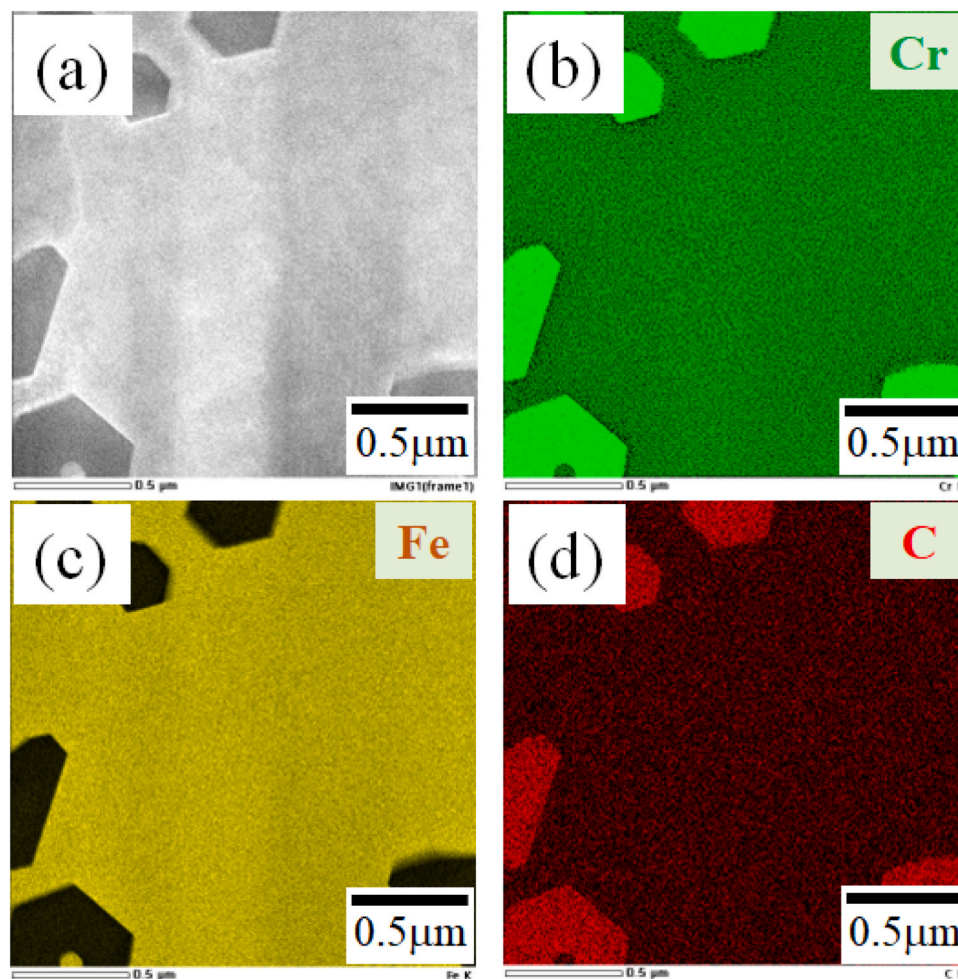


Fig. 6. Results of STEM-EDS analysis of the eutectic structure the melt pool of  $\sim 6$  mm in diameter, showing nonexistence of fine precipitates of chromium carbide in the matrix phase of  $\gamma$ -Fe.

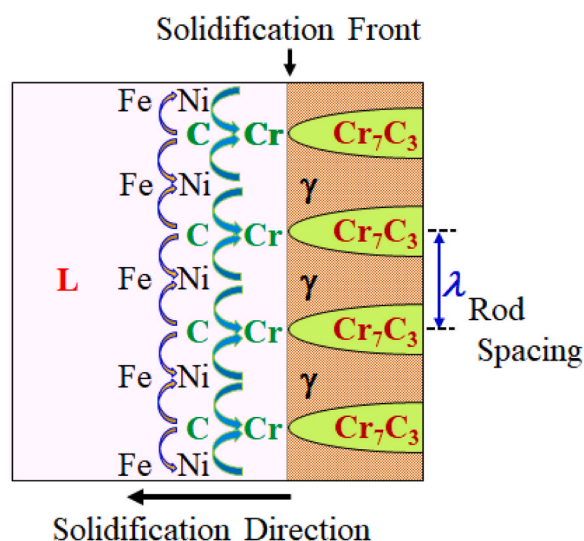


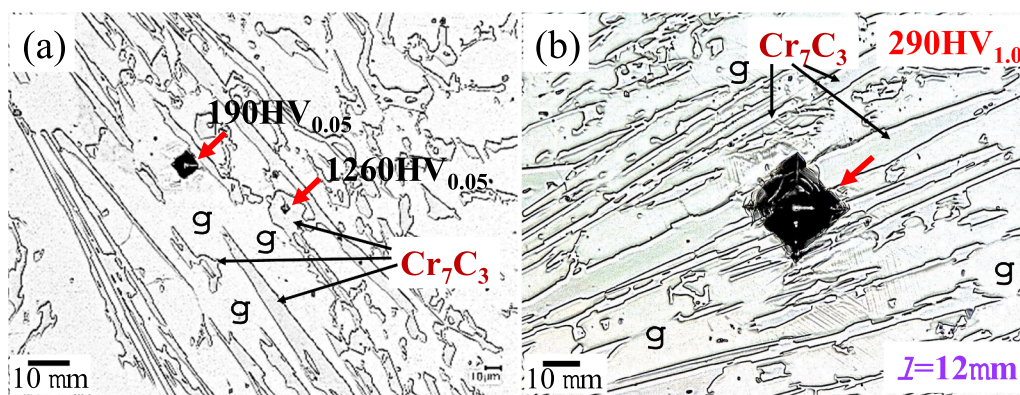
Fig. 7. Schematic illustration of a eutectic solidification,  $L \rightarrow \gamma + Cr_7C_3$ , and diffusion of atoms in the liquid which controls the rod spacing.

prediction based on Fig. 1(d). It is to be noted that the  $\gamma$ -to- $\alpha$  transformation and the change of the carbide type during cooling did not occur even when cooled at an extremely slow rate of  $0.2$  °C/s. However,

when the furnace-cooled sample was subjected to a thermal cycle of 4 cycles of holding at  $800$  °C for  $4$  h, XRD analysis detected  $\alpha$ -iron and  $M_{23}C_6$ -type chromium carbide in addition to  $\gamma$ -iron and  $M_7C_3$ -type chromium carbide.

Results of microstructure observation are given in Fig. 3. The sample used here was a melt pool of  $\sim 6$  mm in diameter made by arc-discharge for  $\sim 2$  s on the surface of button-like ingot of room temperature. As seen in Fig. 3(a) and (b), a small number of primary dendrites are formed, and all the rest of the observed area is occupied by fine eutectic colonies. The existence of the primary dendrites corresponds to the primary solidification of  $\delta$ -Fe seen in the phase diagram (Fig. 1(d)). A SEM observation reveals that the colonies have an extremely fine rod-like dual-phase structure (Fig. 3(d)).

In order to analyze the chemical composition of the rods using the STEM-EDS and estimate the volume fraction of the rod-like phase in the eutectic colony, we observed a cross section perpendicular to the longitudinal direction of the carbide rods. This is because in arbitrary cross sections, the results of STEM-EDS analysis are often inaccurate due to the existence of considerably thin sections of the particle or the existence of parts of the particles underneath the surface of the matrix phase (Fig. 4). To observe the cross section perpendicular to the longitudinal direction of the carbide rods using the STEM, a eutectic colony where longitudinal direction of the rods is parallel to the observation surface was chosen, and a thin plate of which thickness direction is parallel to the longitudinal direction of the particles was FIB-milled (Fig. 5(a)), and the thin plate was lifted out from the sample (Fig. 5(b)). The TEM observation in the thickness direction of the FIB-milled lamellar reveals



**Fig. 8.** Solidification structure images of different areas on a section of an ingot sample made by furnace melting and controlled cooling at 2 °C/s. Red arrows indicate Vickers indentation marks with a loading force of (a) 0.05 kg and (b) 1.0 kg.

that the eutectic carbide rods have a polygonal cross-sectional morphology (Fig. 5(c)). The results of the STEM-EDS analysis performed on this cross section clearly show that the carbide rods contain high concentrations of Cr and C and a negligibly low concentration of Fe (Fig. 5(d) to (f)). Ni concentration was also negligibly low in the carbide rods, according to the STEM-EDS analysis result, which is left out of this figure. The results of the XRD and STEM-EDS analyses revealed that the eutectic carbide is of  $\text{Cr}_7\text{C}_3$  type and it has a rod-like morphology with a polygonal cross-sectional morphology. The volume fraction of the eutectic carbide was measured on the cross section, and it was found to be 22.4 %, which is close to the calculated volume fraction of 21.0 % (Fig. 1(d)). The  $\gamma$ -Fe matrix area in Fig. 5(c) was observed and analyzed at a higher magnification, and the results are given in Fig. 6. There are no precipitates in the area of  $\gamma$ -Fe matrix phase, which means that no formation of carbide precipitates occurred during cooling after the eutectic solidification.

From the results described above, it was confirmed that the present alloy has a dual-phase eutectic structure consisting of  $\gamma$ -Fe matrix and a polygonal rod-like eutectic chromium carbide of  $\text{M}_7\text{C}_3$  type with a volume fraction of approximately 20 %. It is well known that the strength of the composite material rises with the increase in the volume fraction of the strong phase and with the decrease in the distance between the particles of the strong phase [12,13]. Because the volume fraction of the eutectic carbide is fixed at approximately 20 % in the present alloy, the parameter that controls the mechanical strength will be the distance between the rod-like eutectic chromium carbide, or rod spacing. The rod spacing will be controlled by the cooling rate during solidification, because during the eutectic solidification, the atoms diffuse in the liquid near the solidification front to form the dual-phase structure, as illustrated in Fig. 7, and the diffusion time or the cooling rate determines the rod spacing,  $\lambda$ . Therefore, we investigated the possibility of considerable increase in strength due to dramatic refinement of eutectic structure that will be obtained by extreme increase in cooling rate.

Fig. 8 shows solidification structure images of an ingot sample made by the furnace melting followed by controlled slow cooling. The Vickers hardness of the  $\gamma$ -Fe matrix phase and the eutectic carbide phase were 190  $\text{HV}_{0.05}$  and 1260  $\text{HV}_{0.05}$ , respectively, as indicated in Fig. 8(a). The measured hardness of the  $\gamma$ -Fe matrix phase is close to that of typical austenitic stainless steels of SUS304 and SUS316 ( $\sim 180$  HV) [16]. The hardness measured in the dual-phase area was 290  $\text{HV}_{1.0}$ , and the rod spacing was 12  $\mu\text{m}$ , as shown in Fig. 8(b). We also measured the Vickers hardness and the rod spacing of other samples made by other methods. Some results are given in Fig. 9, and it can be seen in the figure that the rod spacing varies depending on the sample making method, and the decrease in rod spacing brings about the increase in Vickers hardness.

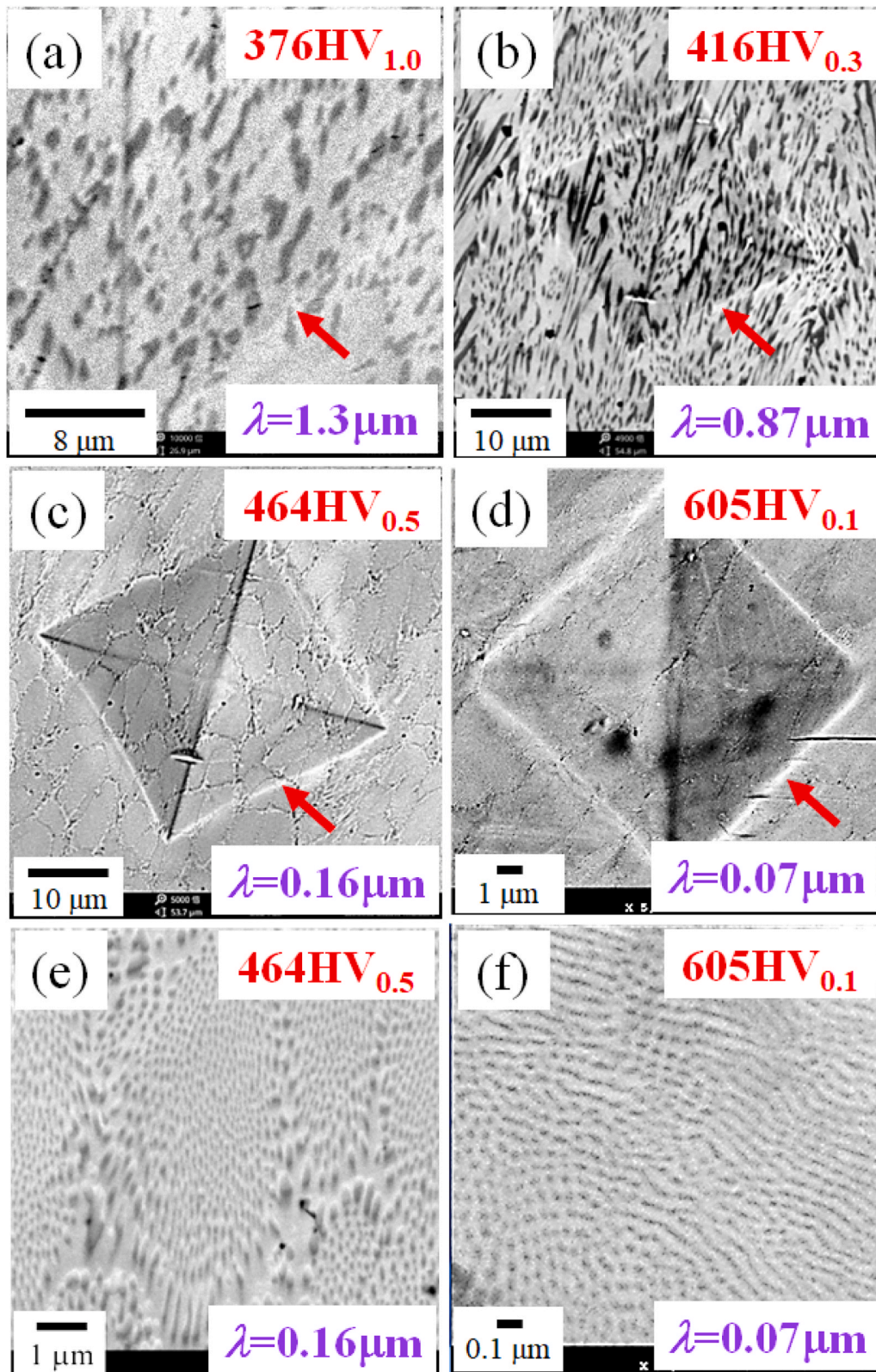
The relation between the rod spacing,  $\lambda$ , and the Vickers hardness,  $\text{HV}$ , is summarized in Fig. 10(a). The decrease in rod spacing strongly affects the increase in hardness, when  $\lambda < 1 \mu\text{m}$ . The effect of the rod

spacing on hardness can be compared to the effect of the grain size on strength, because the phase boundary between the rod-like carbide and the matrix can interrupt the dislocation migration in the matrix phase during plastic deformation like grain boundary. Therefore, we assumed Hall-Petch relationship and performed a regression analysis. The result is depicted in Fig. 10(b), where  $\text{HV}$  lineally increases with the inverse of square root of  $\lambda$ . The relation was described as a regression equation of  $\text{HV} = 67.4 \lambda^{-1/2} + 305$  with a high correlation coefficient of  $R^2 = 0.9009$ , indicating a high accuracy of this regression equation. Vickers hardness of this eutectic alloy increased from  $\sim 300$  to  $\sim 600$  HV as the rod spacing of the eutectic chromium carbide decreased from  $\sim 10$  to  $\sim 0.07 \mu\text{m}$ .

Such fine eutectic structure and high hardness as  $\sim 0.07 \mu\text{m}$  and 600 HV were obtained in a sample made by the laser-remelting method. However, an Inconel 718 superalloy sample made by the laser powder bed fusion process did not exhibit such high hardness, although it had a quite fine solidification structure, as shown in Fig. 11. According to Fig. 11(b), the distance between columnar dendritic cells is approximately 1  $\mu\text{m}$ , which is quite fine compared with the dendritic structure of the present alloy shown in Fig. 3(a). However, hardness of the Inconel 718 superalloy of Fig. 11 was  $\sim 350 \text{ HV}_{1.0}$ , which means that the mechanical strength cannot be always significantly increased by only dramatic refinement of solidification structure. As seen in Fig. 11(b), the grain size or cell colony size is huge, although the solidification structure is quite fine. The formation of such huge cell colonies is due to the epitaxial growth of the cells at the melt pool boundary, as seen in Fig. 11(b). This means that in conventional alloys like Inconel 718 superalloy, the ultrafine solidification structure formed by the additive manufacturing cannot be utilized for the Hall-Petch strengthening. On the other hand, it is expected based on the results shown in Fig. 10 that the present alloy can be Hall-Petch strengthened when it is processed by the additive manufacturing. To verify whether this expectation is valid or not, we planned to build a small prototype of the present alloy using the laser powder bed fusion process and measure the hardness of the prototype. First, we produced powder of the present alloy using a gas atomization process (Mitsubishi Steel MFG. Co., Ltd.). The chemical composition of the powder was Fe-2.1%Cr-32.4 %Cr-6.5 %Ni-0.9 %Si (mass%) with an average diameter of 39  $\mu\text{m}$  and a range of diameter of 20–66  $\mu\text{m}$ . Using this powder, we built a disc-like prototype of with a diameter of 10 mm and a thickness of 0.3 mm using a laser powder bed fusion system (TruPrint 1000, TRUMPF) under conditions of a laser power of  $\sim 60$  to  $\sim 115$  W, a laser spot diameter of 55  $\mu\text{m}$ , and a laser scan speed of  $\sim 400$  to  $\sim 700$  mm/s.

The microstructure of the gas-atomized powder consisted of the primary dendrites and the rod-like eutectic structure (Fig. 12). Vickers hardness of the powder was measured on the cross section of the power particles, and the results ranged between  $\sim 500$  and 620  $\text{HV}_{0.05}$ . The prototype sample had a scaly pattern formed by periodic solidification of





**Fig. 9.** Eutectic structure images of (a) the arc-melted ingot, (b) a melt pool of  $\sim 6\text{ mm}$  in diameter formed on the arc-melted ingot, (c) another melt pool of  $\sim 3\text{ mm}$  in diameter formed on the furnace-melted ingot, and (d) a laser-remelted surface layer of  $\sim 0.1\text{ mm}$  in thickness. Images (e) and (f) are enlarged ones of (c) and (d), respectively. Red arrows indicate a side of the square-shaped Vickers indentation marks. The measured results of the hardness and the interparticle distance are attached to each image.



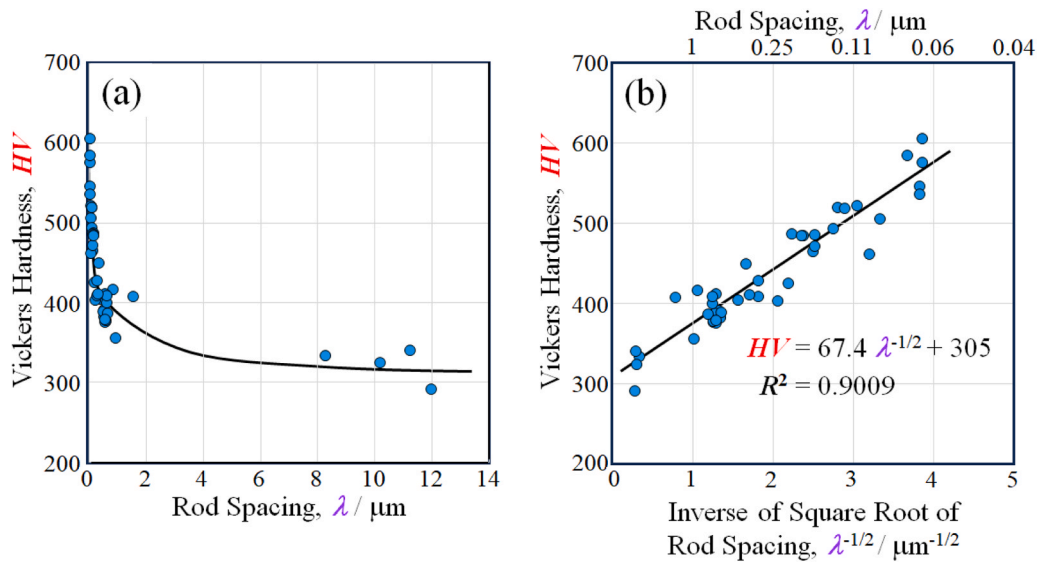


Fig. 10. (a) Effect of rod spacing on Vickers hardness. (b) Linear relationship between Vickers hardness and inverse of square root of rod spacing.

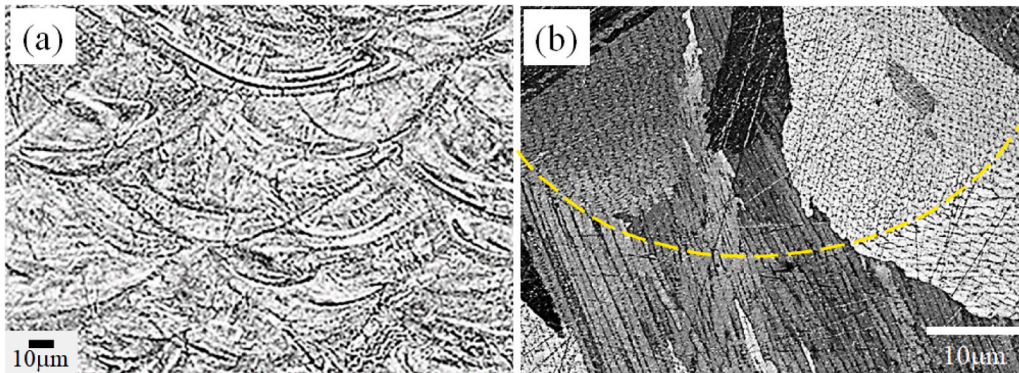


Fig. 11. Microstructures of an Inconel 718 superalloy sample made by the laser powder bed fusion process, showing (a) a scaly pattern formed by periodic solidification of melt pools and (b) dendritic cells and crystal grains growing across the melt pool boundary (dashed line).

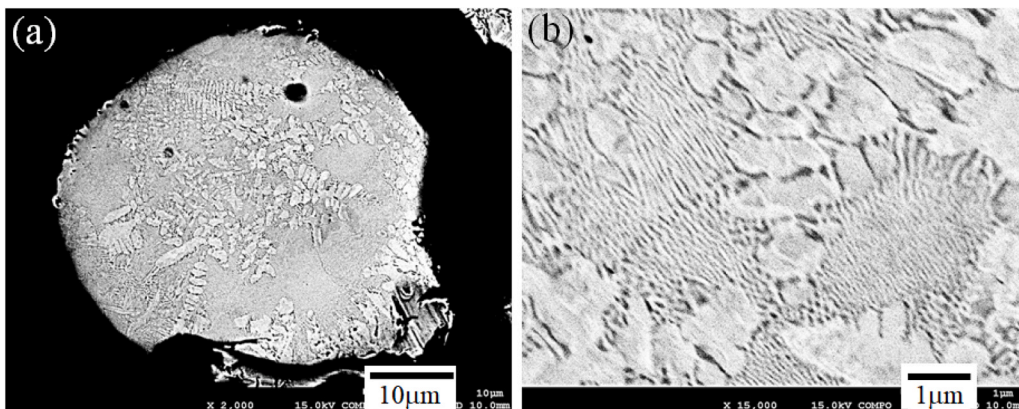
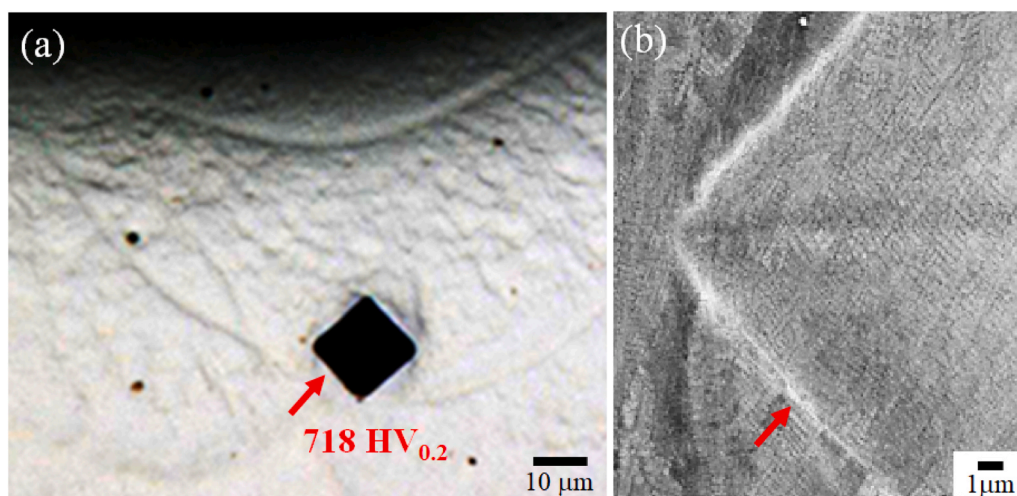


Fig. 12. (a) A SEM image of an entire cross section of the gas-atomized powder. (b) An enlarged image of (a).

melt pools (Fig. 13(a)) and ultrafine dendritic structure formed in the melt pool (Fig. 13(b)). Vickers hardness of the prototype sample was 718 HV<sub>0.2</sub>, twice the hardness of an Inconel 718 superalloy sample produced using the same process. Therefore, it was verified that the present alloy can be Hall-Petch strengthened when processed by laser powder bed fusion, and the hardness can reach ~720 HV.

Why can the present alloy be significantly Hall-Petch strengthened

when it is applied to the laser powder bed fusion process? The reason is the existence of phase boundaries between  $\gamma$ -Fe (Ni) matrix and eutectic chromium carbide rods. The phase boundaries can interrupt dislocation migration and strengthen the alloy. Although the volume fraction of the eutectic carbide is fixed at ~20 % in the present alloy, the total area of the phase boundaries increases with increasing cooling rate. The extremely high cooling rate in the laser powder bed fusion process



**Fig. 13.** Microstructures of the small prototype sample made of the present alloy by using the laser powder bed fusion process, showing (a) a scaly pattern formed by periodic solidification of melt pools and (b) dendritic cells formed in the melt pool. Red arrows indicate a side of the square-shaped Vickers indentation mark. The hardness of this sample was 718 HV.

( $\sim 10^6$  to  $\sim 10^7$  °C/s [15]) leads to an extremely large total area of the phase boundary, which effectively interrupts dislocation migration and significantly Hall-Petch strengthens the alloy. On the other hand, in the laser powder bed fusion process of common alloys like the Ni-based superalloy, the grain size becomes huge due to epitaxial growth at the melt pool boundary, and Hall-Petch strengthening cannot be expected in spite of the ultrafine dendritic structure. Therefore, it can be predicted that many other eutectic alloys will also exhibit significantly high strength, when they are applied to the laser powder bed fusion process.

#### 4. Conclusions

An Fe-based alloy containing 2.0 % C, 33.1 % Cr, 6.4 % Ni and 1.0 % Si (mass%) was found to have an almost full eutectic structure with a small amount of  $\gamma$ -Fe dendrite after solidification. The eutectic structure consisted of the  $\gamma$ -Fe matrix and rod-like eutectic chromium carbide of  $M_7C_3$  type. The carbide rods had a polygonal cross-sectional morphology, and its volume fraction was approximately 20 %. The Vickers hardness of the  $\gamma$ -Fe matrix and the eutectic chromium carbide were 190 HV and 1260 HV, respectively. The hardness measured in the dual-phase eutectic area increased from  $\sim 300$  to  $\sim 600$  HV, as the interparticle distance or rod spacing of the eutectic chromium carbide decreased from  $\sim 10$  to  $\sim 0.07$   $\mu\text{m}$ . The relation between the Vickers hardness,  $HV$ , and the rod spacing,  $\lambda$ , was described as a regression equation of  $HV = 67.4 \lambda^{-1/2} + 305$  with a high correlation coefficient of  $R^2 = 0.9009$ . When this alloy was applied to the laser powder bed fusion process to make a small prototype, the as-built prototype exhibited a considerably high hardness of  $\sim 720$  HV, twice the hardness of an Inconel 718 Ni-based superalloy sample produced using the same process.

#### CRedit authorship contribution statement

**Kiyotaka Matsuura:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Conceptualization. **Genki Saito:** Investigation. **Norihito Sakaguchi:** Investigation, Funding acquisition. **Naomi Kitagawa:** Investigation. **Rutkowski Pawel:** Investigation. **Dariusz Kata:** Writing – review & editing.

#### Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Norihito Sakaguchi reports financial support was provided by Hokkaido University, Faculty of Engineering, Joint research funds from Mitsubishi Steel Mfg Co Ltd, No. PC2525A039. Kiyotaka Matsuura reports a relationship with Mitsubishi Steel Mfg Co Ltd that includes: consulting or advisory. Kiyotaka Matsuura has patent "Production method of a stainless steel" pending to assignee. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgement

The authors gratefully acknowledge the work of past and present members of the laboratory at Hokkaido University: M.S. Yukiko Tanaka, B.S. Emiko Obari, B.S. Koji Yamada and M.S. Michiko Tani. The arc-melted sample was made at Hokkaido Bureau Welding Engineering Evaluation Committees of The Japan Welding Engineering Society. The laser powder bed fusion of the Inconel 718 sample was performed at NTT DATA XAM Technologies Corporation. The laser powder bed fusion of the small prototype of the present alloy was performed at Washin Sangyo Co., Ltd. A part of this work was supported by "Advanced Research Infrastructure for Materials and Nanotechnology in Japan (ARIM)" of the Ministry of Education, Culture, Sports, Science and Technology (MEXT) at Hokkaido University.

#### References

- [1] T.M. Pollock, S. Tin, Nickel-Based superalloys for advanced turbine engines: chemistry, microstructure and properties, *J. Propuls. Power* 22 (2) (2006) 361–374, <https://doi.org/10.2514/1.18239>. (<https://arc.aiaa.org/doi/abs/10.2514/1.18239>).
- [2] E. Akca, A. Gürsel, A review on superalloys and IN718 Nickel-Based INCONEL superalloy, *Period. Eng. Nat. Sci. (PEN)* 3 (2015).
- [3] T. Murakumo, T. Kobayashi, Y. Koizumi, H. Harada, Creep behaviour of Ni-base single-crystal superalloys with various  $\gamma'$  volume fraction, *Acta Mater.* 52 (12) (2004) 3737–3744, <https://doi.org/10.1016/j.actamat.2004.04.028>. (<https://www.sciencedirect.com/science/article/pii/S1359645404002447>).
- [4] I.G. Akande, O.O. Oluwale, O.S.I. Fayomi, O.A. Odunlami, Overview of mechanical, microstructural, oxidation properties and high-temperature applications of superalloys, *Mater. Today. Proc.* 43 (2021) 2222–2231, <https://doi.org/10.1016/j.matpr.2020.12.523>. (<https://www.sciencedirect.com/science/article/pii/S2214785320402408>).
- [5] Z. Xiong, I. Timokhina, E. Pereloma, Clustering, nano-scale precipitation and strengthening of steels, *Prog. Mater. Sci.* 118 (2021) 100764, <https://doi.org/10.1016/j.pmatsci.2020.100764>. (<https://www.sciencedirect.com/science/article/pii/S0079642520301286>).



- [6] A.F. Padilha, R.L. Plaut, P.R. Rios, Annealing of Cold-worked austenitic stainless steels, *ISIJ Int.* 43 (2) (2003) 135–143, <https://doi.org/10.2355/isijinternational.43.135>.
- [7] H. Aghamohammadi, R. Jamaati, A new 1.1 GPa ultra-high strength ferritic stainless steel designed by synergistic strengthening of martensite and strain hardening, *Mater. Chem. Phys.* 337 (2025) 130585, <https://doi.org/10.1016/j.matchemphys.2025.130585>.
- [8] N. Soldevilla, O. Caballero, Correlation of secondary dendrite arm spacing with the mechanical behaviour of cast 718 alloy, in: E. Ott, A. Banik, X. Liu, I. Dempster, K. Heck, J. Andersson, J. Groh, T. Gabb, R. Helmink, A.T.M.S. Wusatowska-Sarnek (Eds.), 8th International Symposium on Superalloy 718 and Derivatives, The Minerals, Metals & Materials Society, 2014. ([https://www.tms.org/superalloys/10.7449/2014/Superalloys\\_2014\\_757\\_768.pdf](https://www.tms.org/superalloys/10.7449/2014/Superalloys_2014_757_768.pdf)).
- [9] A. Kurdi, A. Aldoshan, F. Alshabouna, A. Alodadi, A. Degnah, H. Alnaser, T. Tabbakh, A.K. Basak, Investigation into the microstructure and hardness of additively manufactured (3D-Printed) inconel 718 alloy, 16, *Materials* 16 (6) (2023 Mar) 2383, <https://doi.org/10.3390/ma16062383>, (<https://pubmed.ncbi.nlm.nih.gov/36984263/>), 16.
- [10] G. Liu, S. Winwood, K. Rhodes, S. Biroscas, The effects of grain size, dendritic structure and crystallographic orientation on fatigue crack propagation in IN713C nickel-based superalloy, *Int. J. Plast.* 125 (2020) 150–168, <https://doi.org/10.1016/j.ijplas.2019.09.010>. (<https://www.sciencedirect.com/science/article/abs/pii/S0749641919303948?via%3Dihub>).
- [11] C. Chen, J. Wang, H. Liao, Z. Ren, S. Yin, Laser additive manufacturing of Single-Crystal superalloy component: from solidification mechanism to grain structure control, in: P. Cavaliere (Ed.), *Laser Cladding of Metals*, Springer, Cham, 2020 November, [https://doi.org/10.1007/978-3-030-53195-9\\_5](https://doi.org/10.1007/978-3-030-53195-9_5).
- [12] L. Wang, B. Ye, W. Huang, W. Ding, Theoretical model of yield strength for eutectic colony microstructure materials, *Scr. Mater.* 231 (2023) 115443, <https://doi.org/10.1016/j.scriptamat.2023.115443>. (<https://www.sciencedirect.com/science/article/pii/S1359646223001677>).
- [13] A.J. Ardell, Precipitation hardening, *Metall. Trans. A* 16 (12) (1985) 2131–2165, <https://doi.org/10.1007/BF02670416>. (<https://doi.org/10.1007/BF02670416>).
- [14] L.E. Ramirez-Vidaurri, M. Castro-Román, M. Herrera-Trejo, K.L. Fraga-Chavez, Secondary dendritic arm spacing and cooling rate relationship for an ASTM F75 alloy, *J. Mater. Res. Technol.* 19 (2022) 5049–5065, <https://doi.org/10.1016/j.jmrt.2022.06.146>. (<https://www.sciencedirect.com/science/article/pii/S2238785422010080>).
- [15] P.A. Hoopes, Melt pool temperature and cooling rates in laser powder bed fusion, *Addit. Manuf.* 22 (2018) 548–559, <https://doi.org/10.1016/j.addma.2018.05.032>. (<https://www.sciencedirect.com/science/article/pii/S221486041830188X>).
- [16] S. Hattori, R. Ishikura, Revision of cavitation erosion database and analysis of stainless steel data, *Wear* 268 (1) (2010) 109–116, <https://doi.org/10.1016/j.wear.2009.07.005>. (<https://www.sciencedirect.com/science/article/pii/S0043164809004566>).