Preparation and characterization of spherical nickel silicide powder by inductively coupled plasma spheroidization for additive manufacturing

Foysal Kabir Tareq[*,1], Ragnhild E. Aune[1,2], Geir Grasmo[1], Naureen Akhtar[1], and Tor Oskar Sætre[1]

[1]Department of Engineering and Science, Faculty of Engineering Sciences, University of Agder, Grimstad, Norway
[2]Department of Materials Science and Engineering, Norwegian University of Science and Technology (NTNU), Trondheim, Norway

*Corresponding author: foysal.tareq@uia.no

Keywords: Spherical metal powder, nickel silicide, plasma spheroidization, additive manufacturing

---

Metal alloy powder with spherical-shaped morphology, high flowability, and packing density are the main requirements for metal-based Additive Manufacturing (AM). Among metal alloys, nickel silicide is considered as a potential candidate due to its unique properties such as high melting point, good electrical conductivity, as well as high corrosion and wear resistance. However, the fabrication of spherical nickel silicide powder has proven to be a challenging task. In the present work, spherical NiSi16 alloy powders were synthesized by Inductively Coupled Plasma Spheroidization (ICPS). The influence of the feed rate on the properties of the as-prepared powder was investigated using different analytical techniques to evaluate the particle morphology, particle size distribution, oxygen content, bulk density, fluidity, and spheroidization rate. The results showed some unique advantages of the ICPS technology in the preparation of spherical nickel silicide powder that is believed to be well suited for AM.

1. Introduction

Recently, the application of metal silicides has gained more attention among researchers and various industries especially in additive manufacturing (AM) due to their excellent properties such as excellent corrosion and wear resistance, high strength and high-temperature oxidation resistance.[1-3] Such popular properties are unfavorably associated with characteristics of high melting point, high hardness, and low fracture toughness at low temperatures which pose challenges to the application of these materials in AM.[3-8] Additions of a second or third element are a good way to improve the properties.[1]

Nickel silicide is one of the well-known metallic silicides with excellent physical and functional properties. Composites with the Ni element is a good way to improve the properties of silicide-based materials.[1] However, due to the high melting point and hardness, powder metallurgical technologies are normally the most effective way for producing nickel silicides. Powders synthesized by traditional methods may have irregular size and shape, low powder flowability, and packing density. Though irregular-shaped powders may possess good compressibility, spherical-shaped powders typically have better packing density, flowability, and lower inter-particle friction and therefore are commonly specified for AM.[5,9] In the past few years, plasma spheroidization techniques have been developed to produce spherical metal powders.[10-14]

Among plasma spheroidization technologies, inductively coupled plasma spheroidization (ICPS) is a promising technology because it has a long reaction zone and residence time, which are favorable for the endothermic melting of metal powders. Various spherical metal powders have been produced by the ICPS technology.[5,15-17] For example, Qian qin et al. [5] prepared spherical shaped Ta powder from irregularly shaped powders using inductively coupled plasma processing technology. The obtained Ta powder exhibited improved apparent density, tap density, and flowability.

The development and production of existing and new material powders consisting of spherical particles with the aim of entering new applications using ICPS technology is complicated. Therefore, various parameters such as feed rate, gas flow rate, residence time, and pressure need to be optimized in ICPS for the transformation of irregularly shaped particles to spherical shaped particles.

Up til now, no studies on the preparation of spherical nickel silicide powder using ICPS technology have apparently been reported. In the present work, the spheroidization of NiSi16 was performed by ICPS with NiSi16 feedstock consisting of different particles sizes of irregular shapes. The influence of the feed rate of the feedstock material on the ICPS was investigated to provide a technical condition for the preparation of high-quality spherical NiSi16 powder for AM. The results from a systematic investigation of the powder morphology, phase, crystal structure, particle size distribution, oxygen content, bulk density and flowability were studied.

2. Experimental procedure

2.1 powder

NiSi16 feedstock powder (NiSi16-Feed) consisting of different particles sizes (d_{10}=47.3μm, d_{50}=62.1μm and d_{90}=91.5μm) with irregular shapes was obtained from ELKEM Technology, Norway.

2.*2 Experimental*

The spheroidization of NiSi16-Feed was performed on a TEKSPHERO-15 (Tekna Co. Ltd Canada) Inductively Coupled Plasma Spheroidization (ICPS) system. The ICPS procedures are briefly described here. Firstly, the ICPS system was evacuated. After evacuating the system, argon as a central gas and a secondary gas of hydrogen were purged to the system. Further, the sheath gas (argon) was purged to cool down the quartz tube of the plasma system. First, plasma was generated in the tube. After that, the NiSi16-Feed powder particles were fed into the plasma torch through a vibration-type powder feeder. Particles were melted and formed liquid droplets at the high-temperature plasma torch zone. Finally, these droplets flew out of the plasma torch zone and solidified in the argon gas to form spherical particles. The ICPS treatment was performed at a power of 15 kW. The experimental parameters are summarized in Table 1.

Table 1. Experimental parameters of ICPS treatment

Parameters	Values
Plasma power (kW)	15
Reactor pressure (psi)	15
Sheath gas (slpm)	35
Central gas (slpm)	10
Secondary gas (slpm)	4
Carrier gas (slpm)	5
Feed rate (g/min)	6, 8, 10, 12

2.3 Characterization of powders

The phase and structural characteristics of powders were determined by an X-ray diffractometer (XRD, Bruker) with Cu-Kα radiation. The morphology and microstructure of powders were characterized by JSM-7200F field emission scanning electron microscopy (FE-SEM, JEOL) equipped with a back-scattered electron detector (BED). The elemental distribution was determined by the energy-dispersive X-ray spectroscopy (EDS) technique in SEM equipped with BED. The particles size distribution (PSD) of powders was measured by a particles size analyzer (Malvern, Mastersizer 3000). The apparent density and flowability of powders were measured by a calibrated hall flowmeter.

3. Results and discussion

The spherical NiSi16 powder was prepared by ICPS treatment of the NiSi16-Feed powder. A schematic illustration of the ICPS process is shown in Figure 1a. The ICPS treatment was carried out consisting of feeding NiSi16-Feed powder directly into the plasma torch with a different feed rate (6, 8, 10, and 12 g/min). The particles were vaporized at the high-temperature plasma zone and solidified as spherical particles after flying out from the plasma zone. The obtained powder from the ICPS reactor was indexed as NiSi16-X (X represents the feed rate, 6/8/10/12 g min^{-1}).

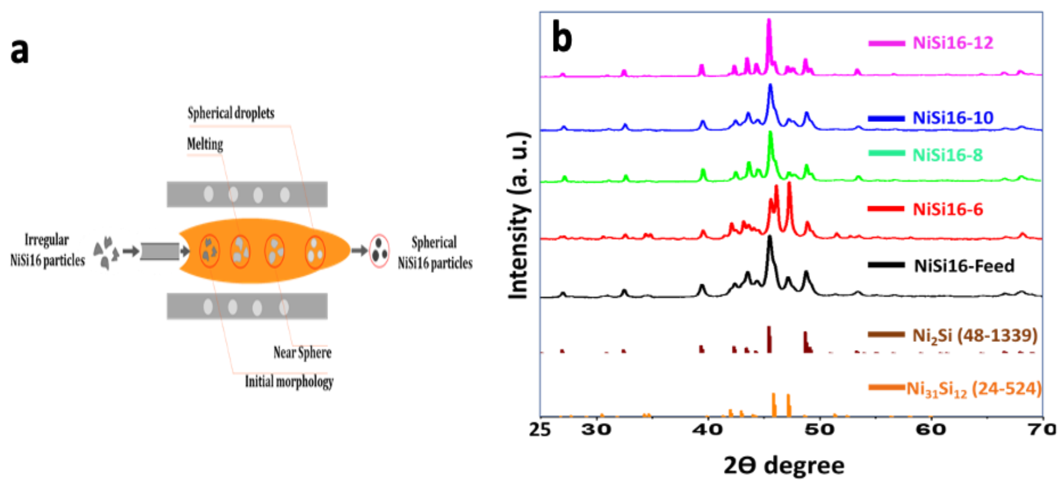

Figure 1. (a) Schematic diagram of the ICPS process of NiSi16 powder, (b) XRD diffraction patterns of NiSi16-Feed and NiSi16-X powders

The phase and crystal structure of the NiSi16-Feed and NiSi16-X powders were analyzed by powder X-ray diffractometer (XRD) and the results are shown in Figure 1b. The XRD diffraction pattern indicates the presence of Ni_2Si (pdf no. 48-1339) and $Ni_{31}Si_{12}$ (pdf no. 24-524) phases in the NiSi16-Feed powder. After the ICPS treatment, the XRD diffraction peaks of the NiSi16-X powders are similar to the diffraction peaks of the NiSi16-Feed powder, indicating that the ICPS treatment did not affect the phase composition of the NiSi16 powders. However, compared to the NiSi16-Feed, the full width at half maximum (FWHM) of diffraction peaks of NiSi-X powders are increased, which indicates that the crystallinity of NiSi16 powder decreases during ICPS treatment. The crystallinity of NiSi16 powder decreases due to the rapid cooling and solidification of molten NiSi16 powder during ICPS treatment.[18]

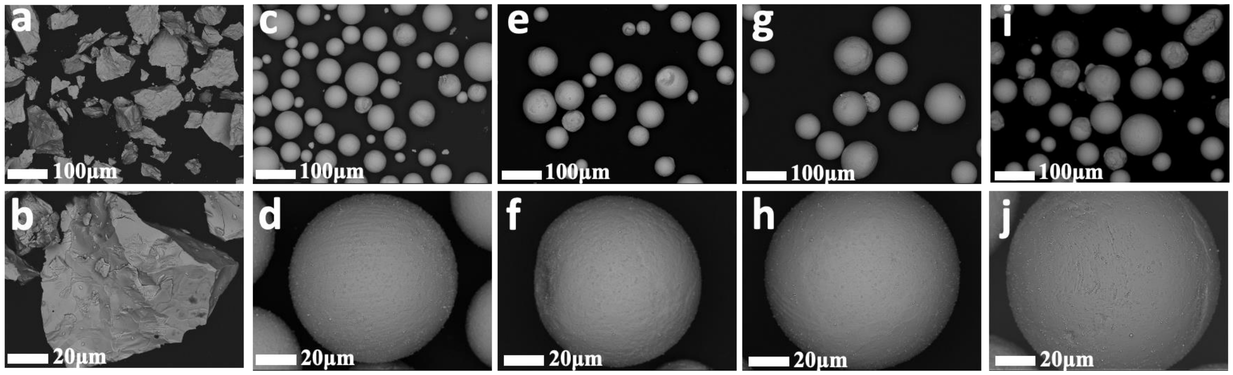

Figure 2. Scanning electron microscopy images of (a, b) NiSi16-Feed, (c, d) NiSi16-6, (e, f) NiSi16-8, (g, h) NiSi16-10, and (i, j) NiSi16-12

Further, the morphology and microstructure properties of the NiSi16-Feed and NiSi16-X powders were studied by SEM and the results are shown in Figure 2. As shown in SEM images of NiSi16-Feed powder (Figure 1a, b), the particles are irregular in shape with sharp edges. After the ICPS treatment, the irregular NiSi16 particles are transformed to spherical particles with a smooth surface (Figure 2c-j). In the ICPS process, the particles could absorb heat energy during passes through the high-temperature plasma zone, resulting in the transformation of the solid phase to liquid droplets. The irregular NiSi16-Feed particles melted and condensed into spherical NiSi16 particles with a smooth surface under the surface tension action.

When the powder feeds to the ICPS process with a lower feeding rate, the particles are spheroidized nearly 100% with a few numbers of satellites for 6 g min^{-1} (Figure 2c, d), 8 g min^{-1} (Figure 2e, f), and 10 g min^{-1} (Figure 2g, h). Furthermore, when the feed rate increases to 12 g min^{-1}, the irregular shape, and satellites of particles are significantly increased (Figure 2i, j). It is suggested that the observation can be explained by the melting process of the feedstock particles [19-21] A particle in the ICPS process should absorb sufficient heat to melt under the operating condition.[22] When the powder was fed to the ICPS system at a low feed rate (6-10 g min^{-1}), all the particles could absorb sufficient heat energy to melt completely, resulting in maximum efficiency of spheroidization.[19] However, when the powder was fed to ICPS at a high feed rate (12 g min^{-1}), all the particles could not absorb sufficient heat energy to melt completely, resulting in a reduction of spheroidization efficiency and thus the quality.[19] However, a slow feed rate could result in lower packing density and poor flowability due to every particle absorbing too much heat. This may result in smaller particles size distributions..[19] Therefore the optimum feed rate is very important to meet maximum efficiency and quality.

Figure 3 shows the cross-section SEM images and elemental distribution results of the NiSi16-Feed and NiSi16-X powders. As shown in cross-section SEM images (Figures 3a, b), two phases (bright and dark part) are observed in the particle of NiSi16-Feed powder. The EDS-point analysis result (Figure 3c) indicates that the bright part has nearly 15.3 wt% (26 at%) Si and the dark part has nearly 18.5 wt% (30.7 at%) Si, which corresponds to the $Ni_{31}Si_{12}$ and Ni_2Si phases, respectively. After plasma spheroidization, similar to the NiSi16-Feed powder, two phases are observed in the cross-section images of the NiSi16-X particle, demonstrating that the ICPS treatment did not affect the phase composition of the NiSi16 powder. Further, the EDS point analysis results indicate that all the NiSi16-X powders have similar elemental distribution to the NiSi16-Feed powder, demonstrating that the ICPS treatment did not affect the elemental composition of NiSi16 powder. These results are strongly evident in the XRD results.

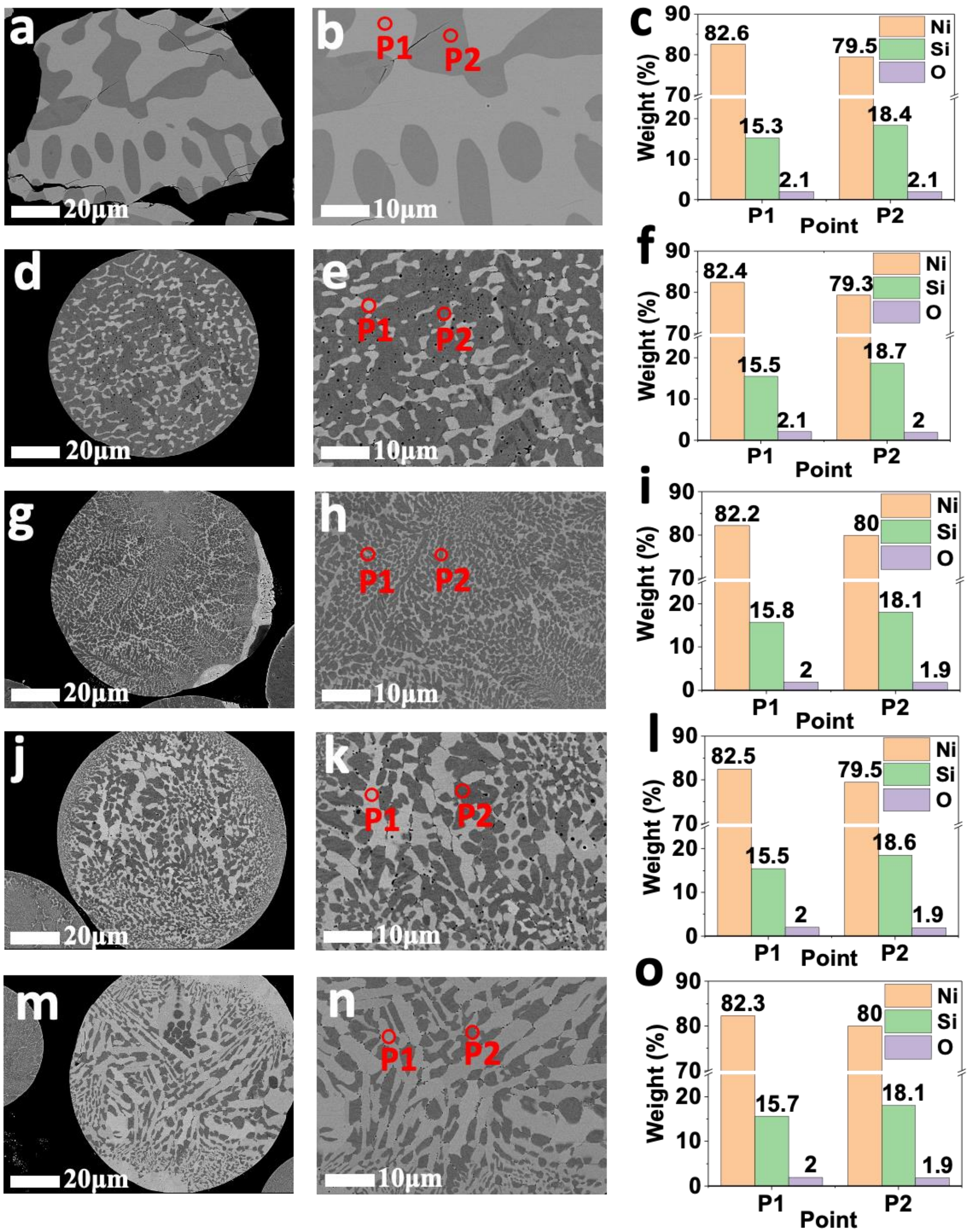

Figure 3. (a) SEM cross-section image, (b) high resolution SEM cross-section image, (c) elemental distribution of NiSi16-Feed. (d) SEM cross-section image, (e) high resolution SEM cross-section image, (f) elemental distribution of NiSi16-6. (g) SEM cross-section image, (h) high resolution SEM cross-section image, (i) elemental distribution of NiSi16-8. (j) SEM cross-section image, (k) high resolution SEM cross-section image, (l) elemental distribution of NiSi16-10. (m) SEM cross-section image, (n) high resolution SEM cross-section image, (o) elemental distribution of NiSi16-12.

The particle size distributions (PSD) was obtained by a particle size analyzer (Mastersizer 3000) and the results are shown in Figure 4a. As shown in the PSD result of NiSi16-Feed powder, the mean particle size varies from 47.3 µm (d_{10}) to 91.5 µm (d_{90}) with a mean (d_{50}) particle size diameter of 62.1 µm. After the ICPS treatment, compared to the NiSi16-Feed, the mean particle size is reduced to 51.0, 52.8, 57.1, 57.3 µm for NiSi16-6, NiSi16-8 NiSi16-10, NiSi16-12 powders, respectively. The mean particle size range is from 35.8 µm (d_{10}) to 79.3 µm (d_{90}) for NiSi16-6, from 36.8 µm (d_{10}) to 83.5 µm (d_{90}) for NiSi16-8, from 40.2 µm (d_{10}) to 88.5 µm (d_{90}) for NiSi16-8, and from 40.2 µm (d_{10}) to 90.5 µm (d_{90}) for NiSi16-12 powder. After the plasma spheroidization, the mean particle size of the produced powders was reduced.
It is also interesting to notice that the particle size distributions are more to the right of higher size values as the ICPS feed rate increases. The particle diameters are increased at a high feed rate due to the augmented interaction between plasma and particles, which leads to the decrease in plasma energy experienced by the individual particles.[21] As a result, the evaporation of the surface and parts of particles can be lowered with respect to the reduced temperature, which leads to an increase of particles size diameter at the exit of the plasma zone.[21]
The above results and discussion suggest that the irregular NiSi16-Feed powder was successfully spheroidized in the ICPS process and the feed rate greatly influences the NiSi16 powders morphology, microstructure properties as well as particles size distribution.

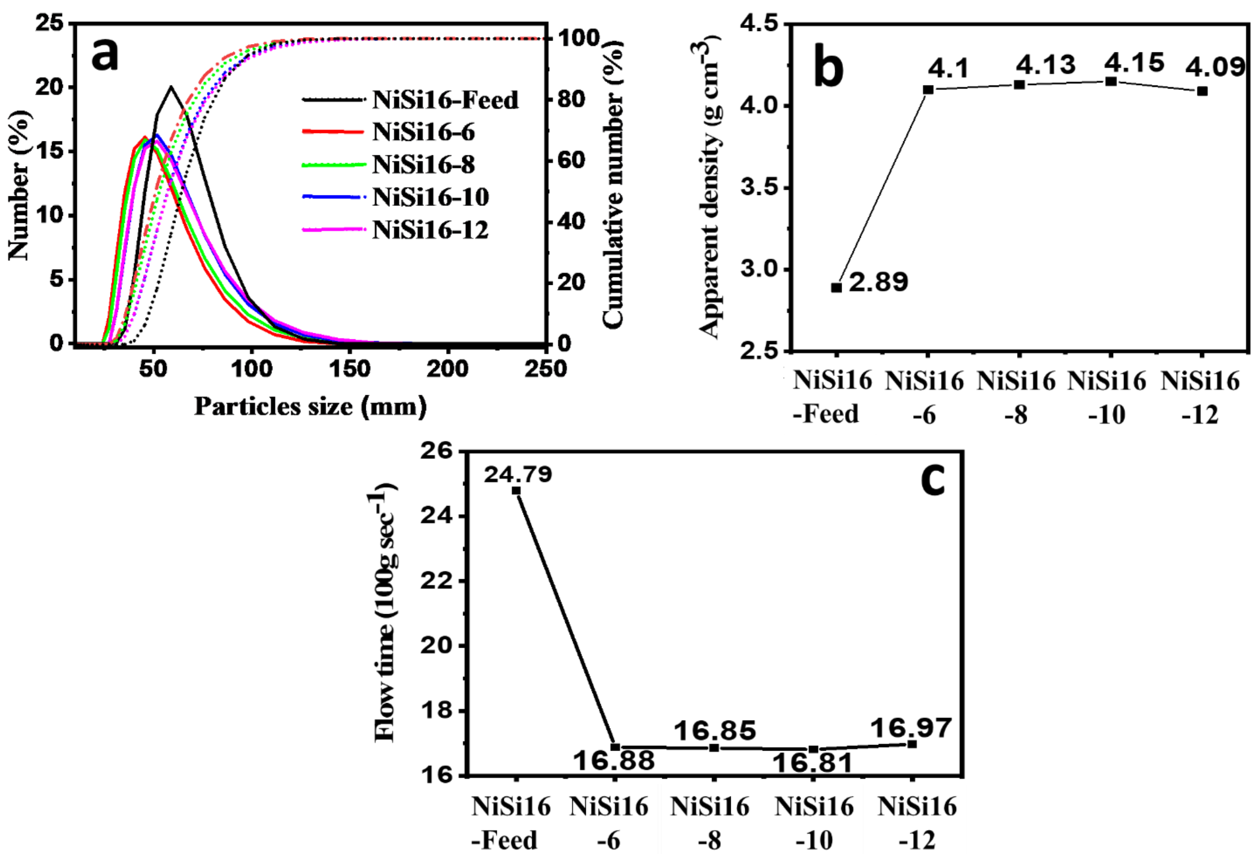

Figure 4 (a) particles size distributions, (b) apparent density, and (c) flowability of NiSi16-Feed and NiSi16-X powders

To investigate the apparent density and flowability of NiSi16-Feed and NiSi16-X powders, a hall flowmeter was used and the results are shown in Figure 4b, c, respectively. Before the ICPS treatment, the NiSi16.1-Feed powder shows a low apparent density (2.89 g cm^{-3}) and poor flowability (100g/24.79s) (Figure 4b and Figure 4c, respectively). After the ICPS treatment, compared to the NiSi16.1-Feed, the apparent density and flowability are significantly improved for all the NiSi16-X powders (Figure 4b, and Figure 4c, respectively). The particles of the feed powder are irregular in shape and size, which leads to higher inter particles friction. As a result, the feed powder shows poor flowability and a lower apparent density. After the ICPS treatment, the particles became smooth and spherical, resulting in reduced particles friction. Therefore, the apparent density and flowability improved significantly. In view of the feed rate effects, the apparent density and flowability increased as a result of increasing the feed rate to 10 g min^{-1}. Further, when the feed rate was increased to 12 g min^{-1} (Figure 4c, d), the apparent density and flowability were reduced due to the presence of satellites as well as the irregular-shaped particles which increased the friction between the particles. A high packing density and flowability of powder are required for additive manufacturing.

4. Conclusion

In summary, starting with the irregular NiSi16 powder, we prepared spherical NiSi16 powders by ICPS process with focusing on powder feeding rates (6, 8, 10, and 12 g min^{-1}). After ICPS treatment, the particles of powders are transformed to spherical shape with a smooth surface and a decent degree of sphericity. The apparent density, and dynamics of flowability of spheroidized powders significantly improved as compared to the feed powder. The particles of powders are spheroidized completely up to the 10 g min^{-1} feeding rate. With the increase of feed rate to 12 g min^{-1}, the spheroidization quality is decreased. After spheroidization, the NiSi16-10 powder showed the maximum apparent density of (4.15 g cm^{-3}) and flowability (100g/16.79s). The present study demonstrated that the ICPS process significantly improved the morphologies, packing density, and flowability of nickel silicide powders which is believed to be well suited for AM.

References

1. Hassannejad, Hossein, et al. "In Situ Formation of Extremely High Corrosion Resistant Ni–Ni 3 Si Nanocomposite Coating Using Spark Plasma Sintering and Subsequent Heat Treatment." Metals and Materials International (2020): 1-11.
2. Chuang, Chenfu, and Shaoliang Cheng. "Fabrication and properties of well-ordered arrays of single-crystalline NiSi 2 nanowires and epitaxial NiSi 2/Si heterostructures." Nano Research 7.11 (2014): 1592-1603.
3. Popovich, A. A., et al. "Fabrication of the Nb–16Si alloy powder for additive technologies by mechanical alloying and spheroidization in electric-arc discharge thermal plasma." Russian Journal of Non-Ferrous Metals 59.6 (2018): 671-676.
4. Tong, J. B., et al. "Fabrication of micro-fine spherical high Nb containing TiAl alloy powder based on reaction synthesis and RF plasma spheroidization." Powder Technology 283 (2015): 9-15.
5. Qin, Qian, et al. "Spheroidization of tantalum powder by radio frequency inductively coupled plasma processing." Advanced Powder Technology 30.8 (2019): 1709-1714.

6. G. Gai, Y. Yang, L. Jin, X. Zou, Y. Wu, Particle shape modification and related property improvements, Powder Technol. 183 (2008) 115–121.
7. Wei, Lufeng, et al. "Microstructure and surface characterization of a selectively dissolved Ni–Ni3Si eutectic alloy." *Journal of Non-Crystalline Solids* 525 (2019): 119576.
8. Soldi, Luca, et al. "Phase diagram and thermodynamic model for the Cu-Si and the Cu-Fe-Si systems." *Journal of Alloys and Compounds* 803 (2019): 61-70.
9. Gai, Guosheng, et al. "Particle shape modification and related property improvements." *Powder Technology* 183.1 (2008): 115-121.
10. Li, Rui, et al. "Fabrication of fine-grained spherical tungsten powder by radio frequency (RF) inductively coupled plasma spheroidization combined with jet milling." *Advanced Powder Technology* 28.12 (2017): 3158-3163.
11. Fu, Zhenhua, et al. "Facile synthesis of nano-particles attached spherical Ti-6Al-4V powder based on plasma spheroidization." *Journal of Alloys and Compounds* 858 (2021): 158313.
12. Polozov, Igor, et al. "Synthesis of titanium orthorhombic alloy spherical powders by mechanical alloying and plasma spheroidization processes." *Materials Letters* 256 (2019): 126615.
13. Hao, Zhenhua, et al. "Preparation of spherical Ti-6Al-4V powder by RF induction plasma spheroidization combined with spray granulation." *Powder Technology* 387 (2021): 88-94.
14. Chenfan, Y. U., et al. "Study on the RF inductively coupled plasma spheroidization of refractory W and W-Ta alloy powders." *Plasma Science and Technology* 20.1 (2017): 014019.
15. Ji, Lina, et al. "Spheroidization by plasma processing and characterization of stainless steel powder for 3D printing." *Metallurgical and Materials Transactions A* 48.10 (2017): 4831-4841.
16. Higashi, Masaya, and Tomomichi Ozaki. "Selective laser melting of MoSiBTiC alloy with plasma-spheroidized powder: Microstructure and mechanical property." *Materials Characterization* 172 (2021): 110888.
17. Goncharov, Ivan, et al. "Microstructure and phase composition of the Nb-Si based in-situ composite from plasma spheroidized powder." *Materials Today: Proceedings* 30 (2020): 545-548.
18. Li, Jing, et al. "Fabrication of spherical Ti-6Al-4V powder for additive manufacturing by radio frequency plasma spheroidization and deoxidation using calcium." *Journal of Materials Research and Technology* 9.6 (2020): 14792-14798.
19. Liu, Xiao-ping, et al. "Spheroidization of molybdenum powder by radio frequency thermal plasma." *International Journal of Minerals, Metallurgy and Materials* 22 (2015): 112-1218
20. Wang, Jian-Jun, et al. "Preparation of spherical tungsten and titanium powders by RF induction plasma processing." *Rare Metals* 34.6 (2015): 431-435.
21. Nam, Jun-Seok, Eonbyeong Park, and Jun-Ho Seo. "Numerical analysis of radio-frequency inductively coupled plasma spheroidization of titanium metal powder under single particle and dense loading conditions." *Metals and Materials International* 26.4 (2020): 491-500.
22. Yuming, Wang, Hao Junjie, and Sheng Yanwei. "Spheroidization of Nd-Fe-B powders by RF induction plasma processing." *Rare Metal Materials and Engineering* 42.9 (2013): 1810-1813.