Thermal plasma spheroidization of Nb-16Si powder alloy obtained by mechanical alloying

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Abstract

Spherical Nb-Si powder alloy is a perspective material to manufacture products for the aerospace industry by additive technologies. Nb-16Si (at.%) powder alloy was prepared by mechanical alloying from pure elemental powders using planetary ball mill Fritsch Pulverisette 4. Spheroidization was carried out on plasma generator based on thermal plasma arc generator with vortex discharge stabilization. Experimental results show that plasma spheroidizing of Nb-16Si powders obtained by mechanical alloying is possible. It is shown that after the spheroidization the particle surface is rough which indicates the cast structure of the material. Three phases having different optical contrast are revealed on microsections: Nb_5Si_3, Nb_3Si and Nb_{ss}, which is confirmed by X-ray diffraction. It is shown that the main peaks in the X-ray graph after MA correspond to a solid solution of niobium with a cubic lattice and the parameter a = 0.333 nm, as well as niobium silicide Nb_5Si_3 with a hexagonal lattice (P63/m) a = 0.7536 nm and c = 0.5249 nm. After spheroidization the hexagonal lattice of niobium silicide Nb_5Si_3 is transformed into a tetragonal lattice (I4/m) with the parameter a = 0.6557 nm and c = 1.186 nm. The other phase components remain unchanged. Copyright © 2018 VBRI Press.

Keywords: Mechanical alloying, in-sute composites, Nb-Si, powder spheroidization, thermal plasma, spherical powder.

Introduction

Modern nickel heat-resistant alloys have operating temperatures of about 1100-1150 °C, which represents 80-85% from the melting point. Further improvement of nickel alloys will not enable increasing the operating temperature significantly due to the relatively low melting point of nickel. Nickel alloys can be replaced by in-sute composites in which the matrix are refractory metals and their silicides will be the intermetallic reinforcement **[1]**. Taking into account the combination of high melting point and low density, niobium silicide Nb_5Si_3 is the ultimate solution among other silicides **[2,3]**. Thus, using heat-resistant materials based on the Nb-Si alloy will enable increasing the operating temperature by 150-200°C **[1]**.

The methods of powder metallurgy, and mechanical alloying in particular, are of considerable interest for obtaining of Nb-Si alloys. Using mechanical alloying one can get particles of powder, homogeneous in structure and composition, with simultaneous formation of a fine grained structure, down to the nanoscale **[4]**. However, currently, there are certain difficulties in obtaining powders with the spherical shape of particles, which complicates to use them in additive technologies. The general requirement to powders for additive technology is a spherical particle shape and particle size distribution of high uniformity. The spherical shape provides a more compact packing of particles in certain volumes and fluidity of the powder with a minimum resistance in the material feed systems **[5-7]**.

Obtaining spherical powders of ceramic materials and refractory compounds using atomization from liquid alloys is rather difficult, that is why it is possible to apply various spheroidization methods. There are several methods of powder spheroidization, one of which uses thermal effects of a plasma stream. High temperature reaching 10000°C in a plasma jet enables melting and vaporizing even the most highly-refractory compounds. Controlling such parameters as powder flow rate, trajectory and plasma flow rate, it is possible to create an optimal mode for getting particles with a spherical shape of compounds with preset composition **[8-12]**.

The paper presents the results of experimental research carried out while processing the powder of Nb-16Si alloy (at.%) produced by mechanical alloying of elemental powders of Nb and Si in the flow of a thermal plasma.

Experimental

Mechanical alloying

Nb-Si-based alloys were prepared by MA of initial powders using a Pulverisette-4 vario-planetary mill (Fritsch GmbH, Germany). High purity Nb (d90 < 200 μm, 99.96% purity; Huizhou Gl Technology Co., LTD, PRC) and Si (d90 <100 µm, 99.95% purity; NevaReaktiv, LLC, Russia) were used as initial components. To prevent oxidation of the initially-formed powder, all operations were handled inside a glove box under a high-purity argon atmosphere. Powders initially nominally composed of Nb and 16 at.% Si were milled for 6 h using a planetary ball mill with hard metal vials and balls under an argon atmosphere and a ball-to-powder mass ratio of 10:1 using a disc rotation velocity of 200 rpm. The main-to-planetary disc rotation velocity ratio was 1:-1.5.

Thermal plasma spheroidization

For the process of Nb-16Si powder spheroidization an plasma generator based on thermal plasma arc generator with vortex discharge stabilization was used. Spheroidization of metal powders in plasma unit is based on heating and melting the initial metallic particles introduced into the plasma jet by carrier gas. The molten particles are simultaneously accelerated down the flame. During the process the molten particles become spheroidized due to surface tension forces. The resulting spherical powder is deposited on the inner walls of the reaction chamber with water-cooled and collected into a hopper of the expected product. A control console controls gas and water flow rates. Experimental research on spheroidization of the Nb-16Si powder was carried out within within torch net power - 7 kW and plasma gas flow - 2 m^3/h. Argon with some additions of hydrogen was used as both the plasma-forming gas and the carrier gas in the experiment.

Characterization

The powder morphology and distribution of elements per volume of powder particle were examined using a scanning electron microscope (Mira 3 Tescan; Tescan Orsay Holding a.s, Czech Republic) at 20 kV equipped with an Oxford INCA Wave 500 add-on device.

The crystal structures of the obtained powders were characterized by X-ray diffraction (XRD) on a Brucker D8 Advance (Bruker Corporation, USA) in CuKα-radiation (λ = 0.15418 nm) at a scanning step of 0.05° (2θ scale) for 0.5 s in the range of 2θ = 30° to 100°. TOPAS software was used to carry out the Rietveld refinement of the XRD patterns and to analyze the crystal structures and calculate the lattice parameters and grain size. The quality of the Rietveld refinement was evaluated in terms of goodness of fit (GOF) and the R factor (R_{wp}). Generally, when GOF is close to 1 and R_{wp} is less than 10%, the result can be considered reliable.

The size of the obtained powders was measured using the laser light scattering method on a Analysette 22 NanoTec (Fritsch GmbH, Germany).

Results and discussion

Nb-16Si particles with fragmented shape and size up to 100 µm (**Fig. 1a**) were obtained by mechanical alloying of the initial powders. During detailed studies of the powder particles it was identified that the particles are agglomerates of micron and submicron particles (**Fig. 1b**). The elemental analysis obtained by energy-dispersive X-ray spectroscopy indicated uniform and homogeneous distribution of each initial element in the particle (**Fig. 1c**). The chemical composition of each powder particles correspond to the initial powder composition.

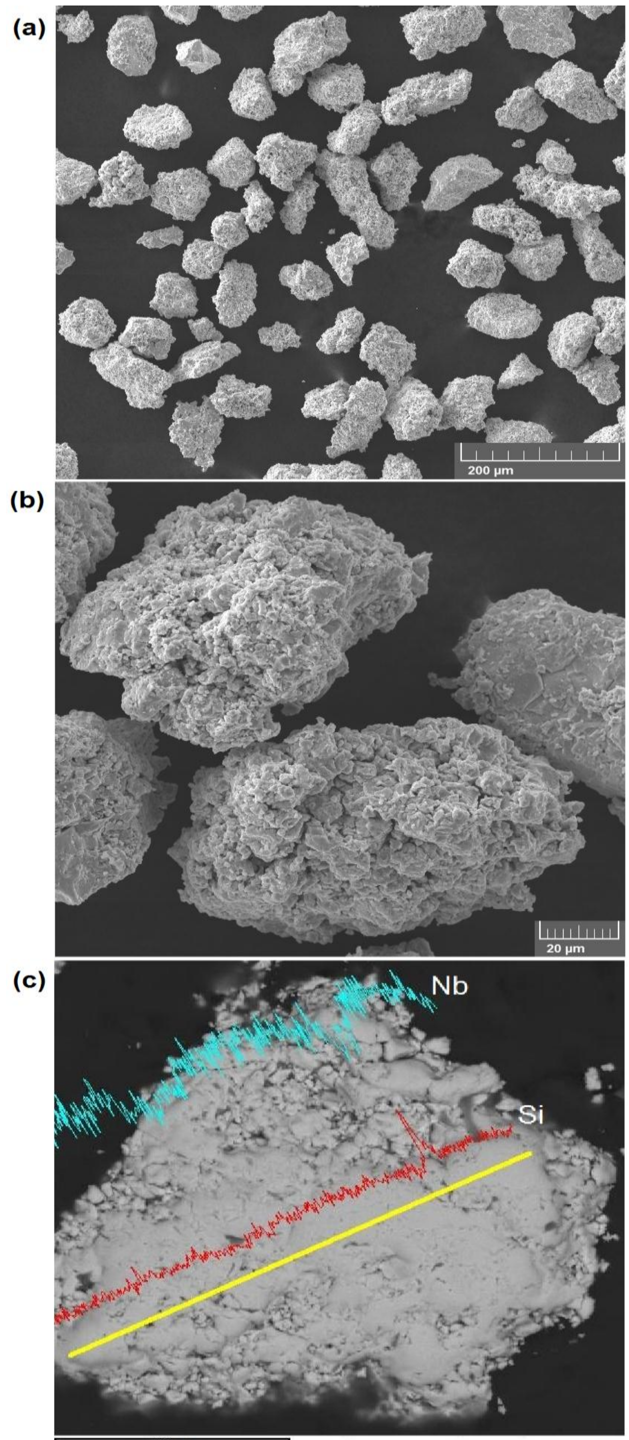

Fig. 1. Morphology of Nb-16Si powder particles after mechanical alloying: a,b) morphology of particles, c) distribution of elements in the volume of the particle.

As described in the introduction, polygonal shaped powders are not suitable for application in additive technology because they have poor flowability and packing density due to internal friction. As a result of a series of experimental tests, it was discovered that spherical powders of Nb-16Si alloy with a high degree of spheroidization (**Fig. 2**) can be obtained in a flow of thermal plasma of argon with some additions of hydrogen generated in an arc jet plasmatron. As the particle enters the plasma flame it gains thermal energy from the plasma and starts melting at the surface if the melting point is reached **[9]**. The melting front propagates inside. Depending on the particle size and the temperature of the plasma, melting might be restricted to the particle's surface or the entire particle may be molten. Small particles may evaporate after complete melting. If a sufficient fraction is molten or if the particle is fully molten, the particle after leaving the flame falls freely through the atmosphere inside the reaction chamber and is ultimately quenched due to the water cooling of the reaction chamber. During this process, the particle becomes spherical due to surface tension forces **[9]**. Due to the fact that the particles were obtained via the non-crucible method, the surface of the particles is uneven (**Fig. 2b, c**) and it reflects the cast structure of the material.

Fig. 3 shows the powder size analysis results for the Nb-16Si particles powders before and after thermal plasma spheroidization. The average size of the powders decreased drastically, from 60 to 45 μm, by plasma treatment. The powder size was reduced due to reflowing and densification of the agglomerates and by evaporation at the powder surface. In the view of the wide distribution of the particle size and their low mechanical strength, which can lead to their degradation into smaller fragments during plasma spheroidization, the evaporation of the smallest particles followed by the condensation of vapor in the form of nanoparticles can be expected. Although 5 mass. % of nano-sized Nb-Si alloys particles caused evaporation followed by condensation of the vaporized Nb-Si atoms, they were easily removed by a sieving method.

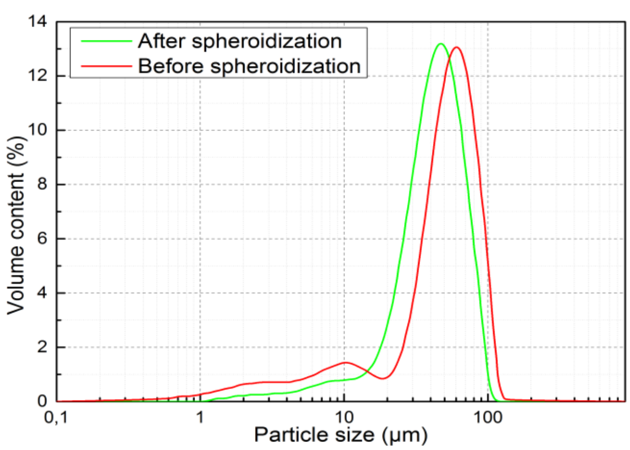

Fig. 3. The powder size analysis results for the Nb-16Si particles powders before and after thermal plasma spheroidization

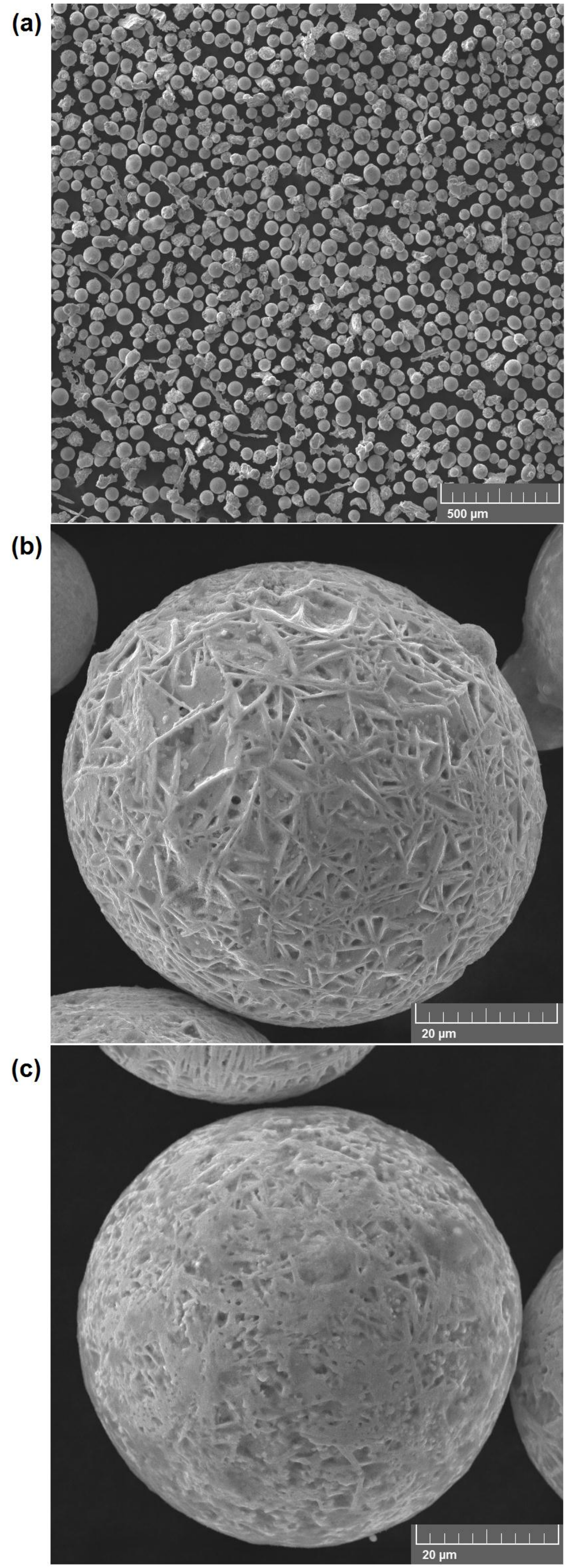

Fig. 2. Morphology of Nb-16Si powder (a) and surface of the particles (b,c) after plasma spheroidization

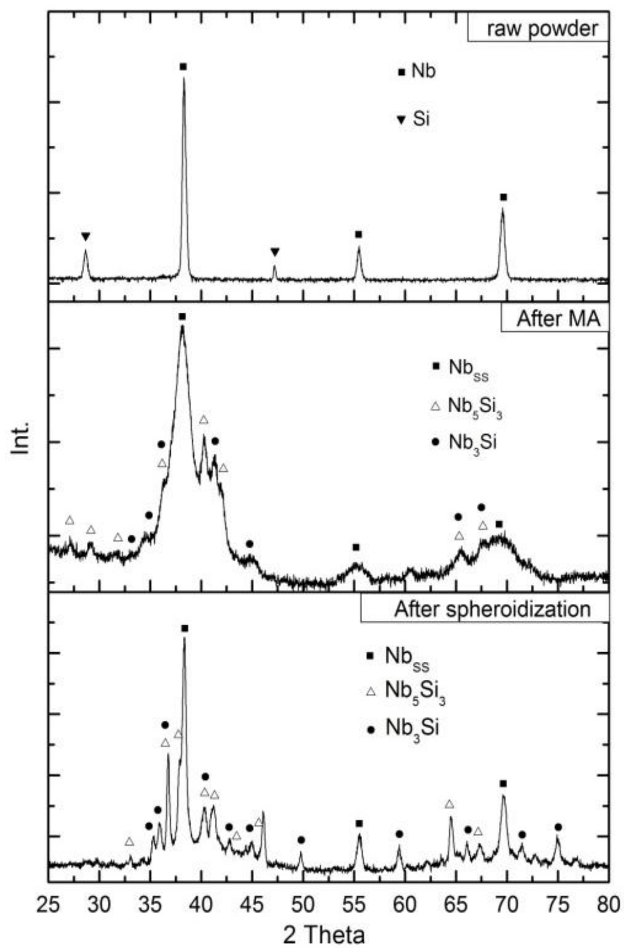

Fig. 4. Changes in the phase composition of Nb-16Si alloy after mechanical alloying and spheroidization.

XRD analysis of the powders obtained by mechanical alloying showed the presence of peaks of the solid solution of niobium (Nb_{SS}) and silicides of niobium - Nb_5Si_3, Nb_3Si (**Fig. 4**). The main peaks in the X-ray graph correspond to a solid solution of niobium with a cubic lattice and the parameter a = 0.333 nm, as well as niobium silicide Nb_5Si_3 with a hexagonal lattice (P63/m) a = 0.7536 nm and c = 0.5249 nm. Broad peaks indicate a strong distortion of the crystal lattice, formed as a result of the intensive mechanical action. After spheroidization the hexagonal lattice of niobium silicide Nb_5Si_3 is transformed into a tetragonal lattice (I4/m) with the parameter a = 0.6557 nm and c = 1.186 nm. The other phase components remain unchanged.

Investigation of polished micro-sections showed that spherical particles had a structure consisting of equiaxed dendrites (**Fig. 5**), whose dimensions at the periphery of particles differed little from those of dendrites in the central parts. It is difficult to identify the order of the axes of such dendrites, as it is not always possible to trace the growth direction. As the size of the particles increases, the distance between dendritic branches grows too, since a longer period of solidification makes the process of coalescence more intensive, causing the dissolution of thin branches and expansion of interaxial intervals.

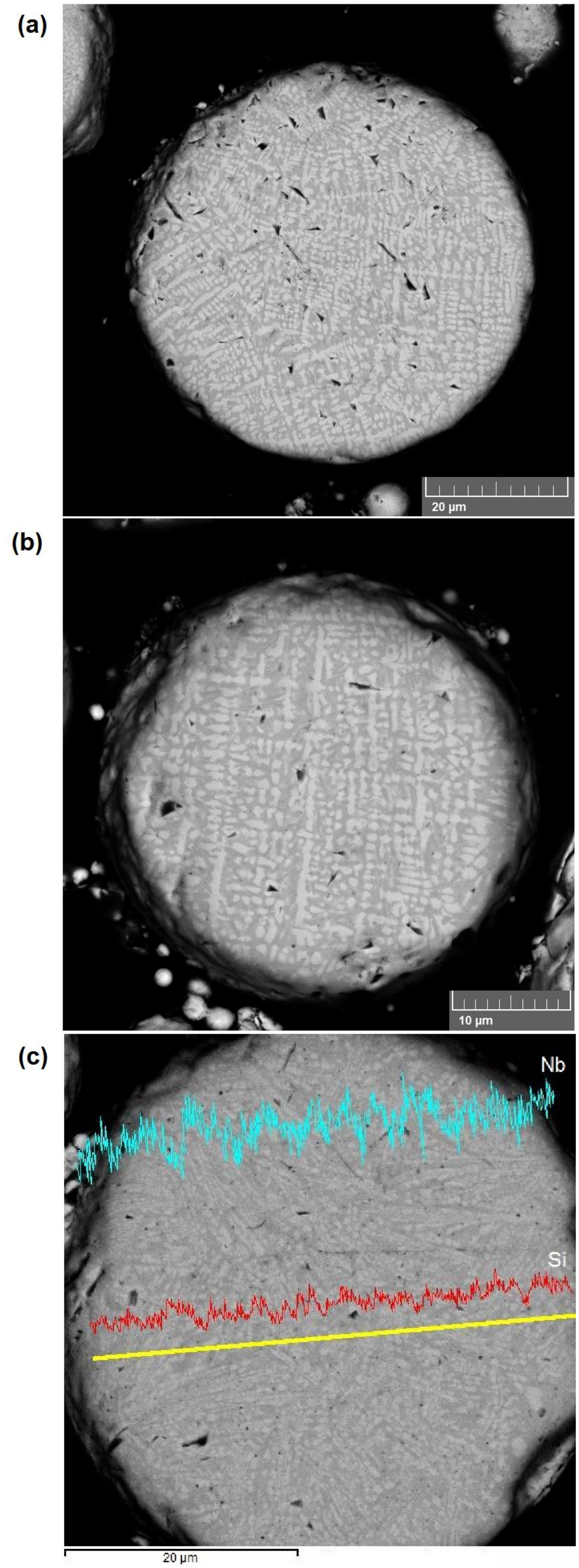

Fig. 5. Microstructure of the Nb-16Si powder particles (a, b) and the distribution of elements in the volume of a particle after plasma spheroidization

The visually identified periodic changes on the surface of a particle (**Fig. 2**) caused by crystallization processes happen at an interval of 4±1 µm, which approximately corresponds to the lateral dimensions of cellular dendrite crystallites that form in the shape of a drop (**Fig. 5**). During radial growth their summits reach the surface of a particle, where there appear grooves delineating them as a result of volumetric shrinkage of the residual molten mass during solidification.

Three phase constituents having different grey levels were discovered on the polished micro-sections: dark grey, grey and light grey (**Fig. 5a, b**). The darkest phase, exhibiting the lowest average atomic number, corresponds to intermetallic Nb_5Si_3, the grey one to Nb_3Si, and the light phase constituent to Nb_{SS}. **Fig. 5c** shows the distribution of the alloying elements in the plane of the polished section. Nb is the basis of the investigated alloy, that is why (according to the law of conservation of mass) in the interdendrite regions the amount of Nb will be smaller than in the regions corresponding to the axes (branches) of the dendrites, which is confirmed with the help of the elements distribution curve. The presence of pores of micron and submicron dimensions in the internal structure of the spherical particles can be connected either with the insufficient melting of the initial highly porous particles, or with the formation of water vapor as a result of hydrogen reduction of metal oxides.

Conclusion

Experimental results show that plasma spheroidizing of Nb-16Si powders obtained by mechanical alloying is possible. It is shown that after the spheroidization the particle surface is rough which indicates the cast structure of the material. The average size of the powders decreased from 60 to 45 µm after plasma treatment. XRD analysis has shown the presence of peaks of niobium solid solution (Nb_{SS}), as well as of niobium silicides Nb_5Si_3, Nb_3Si, which is confirmed by the results of studying the polished micro-sections.

Nb-16Si is initial alloy on which explored the possibility of preparing Nb-Si-alloy spherical particles by mechanical alloying and plasma spheroidization. Spherical Nb-Si powder alloy is a perspective material to manufacture products for the aerospace industry by additive technologies. Further research will be aimed at study the process of selective laser melting Nb-16Si spherical powder alloys and increasing the special characteristics of the Nb-16Si initial alloy by doping with Ti, Cr, Hf, Al, etc.

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Author's contributions

Conceived the plan: Nikolay G. Razumov, Anatoly A. Popovich, Aleksei V. Grigoriev; Performed the expeirments: Nikolay G. Razumov, Andrey V. Samokhin; Data analysis: Nikolay G. Razumov, Andrey V. Samokhin, Aleksei V. Grigoriev; Wrote the paper: Nikolay G. Razumov; Paper examination: Anatoly A. Popovich. Authors have no competing financial interests.

References

1. Drawin, S.; Justin, J.F. *J. AerospaceLab*, **2011**, *3*, 1. [url:http://www.aerospacelab-journal.org/sites/www.aerospacelab-journal.org/files/AL3-06.pdf]
2. Zhao, J.-C.; Bewlay, B.P. *Intermetallics*, **2001**, *9*, 681. **DOI:** 10.1016/S0966-9795(01)00057-7
3. Drawin, S.; Monchoux, J.P.; Raviart, J.L.; Couret, A. *Adv. Mater. Res.*, **2011**, *278*, 533. **DOI:**10.4028/www.scientific.net/AMR.278.533
4. Suryanarayana, C. *Prog. Mater. Sci.*, **2001**, *46*, 1. **PII:** S0079-6425(99)00010-9
5. Wohlers, T. Wohlers Report 2014. 3D Printing and Additive Manufacturing State of the Industry; Wohlers Associates, Inc., **2014**. **ISBN:** 978-0-9913332-0-2
6. Uriondo, A.; Esperon-Miguez, M.; Perinpanayagam, S. *Proc. Inst. Mech. Eng., Part G*, **2015**, *229*, 2132. **DOI:** 10.1177/0954410014568797
7. Gao, W.; Zhang, W.; Ramanujan, D.; Ramani, K.; Chen, Y. *Comput. Aided Des.*, **2015**, *69*, 65. **DOI:** 10.1016/j.cad.2015.04.001
8. Chaturvedi, V.; Ananthapadmanabhan, P.; Chakravarthy, Y.; Bhandari, S.; Tiwari, N.; Pragatheeswaran, A.; Das, A. *Ceram. Int.*, **2014**, *40*, 8273. **DOI:** 10.1016/j.ceramint.2014.01.026
9. Kumar, S.; Selvarajan, V. *Mater. Charact.*, **2008**, *59*, 781. **DOI:** 10.1016/j.matchar.2007.06.011
10. Yang, S.; Gwak, J.-N.; Lim, T.-S.; Kim, Y.-J.; Yun, J.-Y. *Mater. Trans.*, **2013**, *54*, 2313. **DOI:** 10.2320/matertrans.M2013329
11. Zhu, H.L.; Tong, H.H.; Yang, F.Z.; Wang, Q.; Cheng, C. *Adv. Mater. Res.*, **2014**, *1058*, 221. **DOI:** 10.4028/www.scientific.net/AMR.1058.221
12. Pakseresht, A.H.; Rahimipour, M.R.; Vaezi, M.R.; Salehi, M. *Mater. Chem. Phys.*, **2016**, *173*, 395. **DOI:** 10.1016/j.matchemphys.2016.02.028

